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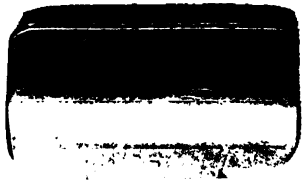
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GENERAL

MEDICAL CHEMISTRY

FOR THE USE OF

PRACTITIONERS OF MEDICINE



BY

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PREFACE.

In the arrangement of this work, it has been deemed advisable to depart, in certain points, from the methods usually followed in chemical text-books. Those portions treating of technical processes have been condensed to a minimum, while the bearings of chemistry upon physiology, hygiene, therapeutics, and toxicology, have been treated of as fully as the limits of the work have permitted. The division of the elements into metals and metalloids has been abandoned as unscientific, and a classification has been adopted which the author believes to possess advantages over those hitherto followed, especially in that it is based upon purely chemical characters.

Organic chemistry has not been considered as a distinct division of the subject, but simply as the chemistry of the compounds of carbon; an arrangement not only logical, but sanctioned by the works of Feser, Schützenberger, and others. The classification of the carbon compounds is based, as far as possible, upon their relations to the different series of hydrocarbons.

The size of the volume being limited, the author has preferred to abstain from the use of illustrations, thinking that the space could be better utilized as it has been. Through mistake of the printer in casting up the copy, he has also been obliged to condense that portion of the work treating of the third and fourth classes of elements more than he wished, and quite out of proportion to the rest of the work.

It is hardly necessary to state that the modern system of notation has been followed. All weights and measures are given in the metric system, and temperatures in degrees of the Centigrade scale.

R. A. W.

766 Madison Avenue, New York,
August 7, 1881.

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GENERAL

MEDICAL CHEMISTRY.

Part 1.

INTRODUCTION.

It is difficult to give at the outset a clear and concise idea of what is understood as chemical science. The best and simplest definition of chemistry is a modification of that given by Webster: That branch of science which treats of the composition of substances, their changes in composition, and the laws governing such changes. It will be seen that the essential character of the science is that it has to deal with *composition*, and in this the line between physical and chemical phenomena is more sharply drawn than that between the individual varieties of the former.

A bar of soft iron is the same in composition, whether it be hot or cold, luminous or non-luminous, magnetized or not magnetized. When, however, it comes under the dominion of chemical action, its composition is changed, and, although the resulting substance contains iron, it differs in its appearance and properties from that metal. Moreover, this change in composition, once brought about, is permanent until another change is wrought by another manifestation of chemical action; on the other hand, the peculiar property communicated to a substance by a physical force is temporary, and only manifested during the action of that force.

However distinct chemical may thus be from physical forces, it is none the less united with them in that grand correlation whose existence was first announced by Grove, in 1842. As, from chemical action, manifestations of every variety of physical force may be obtained: light, heat and mechanical force from the oxidation of carbon; and electrical force from the action of zinc upon sulphuric acid—so does chemical action have its origin, in many instances, in the physical forces. Luminous rays bring about the chemical decomposition of the salts of silver, and the chemical union of chlorine and hydrogen; by electrical action a decomposition of many compounds into their constituents is instituted, while instances are abundant of reactions, combinations, and decompositions which require a certain elevation of temperature for their production. While, therefor,

chemistry in the strictest sense of the term deals only with those actions which are attended by a change of composition in the material acted upon, yet chemical actions are so frequently, nay universally, affected by existing physical conditions, that the chemist is obliged to give his attention to the science of physics, in so far, at least, as it has a bearing upon chemical reactions, to *chemical physics*—a branch of the subject which has afforded very important evidence in the support of theoretical views originating from purely chemical reactions.

General Properties of Matter.

INDESTRUCTIBILITY.—The result of chemical action is change in the composition of the substance acted upon, a change accompanied by corresponding alterations in its properties. Although we may cause matter to assume a variety of different forms and render it, for the time being, invisible, yet in none of these changes is there the smallest particle of matter destroyed. When carbon is burned in an atmosphere of oxygen, it disappears, and, so far as we can learn by the senses of sight or touch, is lost; but the result of the burning is an invisible gas, whose weight is equal to that of the carbon which has disappeared, plus the weight of the oxygen required to burn it.

WEIGHT.—All bodies attract each other with a force which is in direct proportion to the amount of matter which they contain. The force of this attraction exerted upon surrounding bodies by the earth becomes sensible as weight, when the motion of the attracted body toward the centre of gravity of the earth is prevented.

In chemical operations we have to deal with three kinds of weight: *apparent*, *absolute*, and *specific*.

The *apparent weight*, or *relative weight*, of a body is that which we usually determine with our balances, and is, if the volume of the body weighed be greater than that of the counterpoising weights, less than its true weight. Every substance placed in a liquid or gaseous medium suffers a loss of apparent weight equal to that of the volume of the medium so displaced, and is buoyed up to that extent. A cork placed in water sinks until it has displaced a volume of water whose weight is equal to its own. For this reason the apparent weight of some substances may be a minus quantity; thus, if the air contained in a vessel suspended from one arm of a poised balance be replaced by hydrogen, that arm of the balance to which the vessel is attached will rise, indicating a diminution in weight.

The *absolute weight* of a body is its weight in vacuo. It is only determined in very accurate chemical work, by placing the entire weighing apparatus under the receiver of an air-pump, or, in the case of gases, approximately, by first weighing the vessel from which the air has been pumped, and afterward filled with the gas.

By the *specific weight*, or *specific gravity* of a substance, is understood the weight of a given volume of that substance as compared with the weight of an equal volume of some substance taken as a standard of comparison. It is a well-known fact that equal volumes of different substances differ from each other in weight; thus, a litre of hydrogen weighs

0.0896 grams, while the same volume of platinum weighs 21.500 grams, or about 200,000 times as much.

The substance taken as the unit of the specific gravities of solids and liquids is water. The specific weights of gases are usually referred to air as a unit; it is better, however, to adopt hydrogen as such unit (see p. 15). When we say that the specific gravity of sulphuric acid is 1.8, we mean that, volume for volume, sulphuric acid is one and eight-tenths times as heavy as water.

The determination of the specific weight of a substance is frequently of great service. Sometimes it affords a rapid means of distinguishing between two substances similar in appearance; sometimes in determining the quantity of an ingredient in a mixture of two liquids, as alcohol and water; and frequently in determining approximately the quantity of solid matter in solution in a liquid; it is the last object which we have in view in determining the specific gravity of the urine.

An aqueous solution of a solid has a higher specific gravity than pure water, the increase in specific gravity following a regular but different rate of increase with each solid. In a simple solution—one of common salt in water, for instance—the proportion of solid in solution can be determined from the specific gravity. In complex solutions, such as the urine, the specific gravity does not indicate the proportion of solid in solution with accuracy. In the absence of sugar and albumen, a determination of the specific gravity of urine affords an indication of the amount of solids sufficiently accurate for usual clinical purposes. Moreover, as urea is much in excess over other urinary solids, the oscillations in the specific gravity of the urine, if the quantity passed in twenty-four hours be considered, and in the absence of albumen and sugar, indicate the variations in the elimination of urea, and consequently the activity of disassimilation of nitrogenous material.

To determine the specific gravity of substances, different methods are adopted, according as the substance is in the solid, liquid, or gaseous state; is in mass or in powder; or is soluble or insoluble in water.

Solids.—First. The substance is heavier than water, insoluble in that liquid, and not in powder. It is attached by a fine silk fibre to a hook suitably situated on one arm of the balance, and weighed. A beaker full of pure water is so arranged that the substance, still attached to the balance, is immersed in the liquid; in which condition it is again weighed. The second weight will be found to be less than the first. By dividing the weight in air by the loss in water the specific gravity, water=1.00, is obtained. Example:

A piece of lead weighs in air	82.0
A piece of lead weighs in water	74.9
Loss in water	7.1

$$\frac{82.0}{7.1} = 11.55 = \text{sp. gr. of lead.}$$

If the substance be in fine powder, the specific gravity bottle (see p. 4) is used. The bottle, filled with water, and the powder, previously weighed and in a separate vessel, are weighed together. The water is

poured out of the bottle, into which the powder is then introduced, with enough water to fill the bottle completely. The weight of the bottle and its contents is now determined, and is less than the first weight by the weight of the volume of water displaced by the powder. Here again the specific gravity is obtained by dividing the weight of the powder alone by the loss between the first and second weighings.

Second.—If the substance be lighter than water, a sufficient bulk of some heavy substance, whose specific gravity is known, is attached to it and the same method followed, the loss of weight of the heavy substance being subtracted from the total loss. Example:

A fragment of wood weighs	24
A fragment of lead weighs	44
Wood with lead attached weighs	68
Wood with lead attached weighs in water	16
Loss of weight of combination	52
Loss of weight of lead in water	6
Loss of weight of wood	46

$$\frac{24}{46}=0.5217=\text{sp. gr. of wood.}$$

Third.—If the substance be soluble in water, its specific gravity, referred to some liquid in which it is insoluble and whose specific gravity is known, is determined by using that liquid as water is used in 1°. From this the specific gravity of the solid, referred to water, is determined by multiplying the specific gravity so obtained by that of the liquid used. Example:

A piece of potassium weighs	2.576
A specific gravity bottle full of naphtha, sp. gr. 0.758, weighs	22.784
	25.360
The bottle with potassium and naphtha weighs	23.103
Loss	2.257

$$\frac{2.576}{2.257}=1.141\times 0.758=0.865=\text{sp. gr. of potassium.}$$

Liquids.—The specific gravity of liquids is determined by the specific gravity bottle, sometimes called picnometer, or by the spindle or hydrometer.

First.—The method by the bottle is the more accurate, and, if a balance be at hand, easily conducted. A bottle of thin glass is so made as to contain exactly a given volume of distilled water at a given temperature, say 100 c.c. at 15° C.; the weight of the bottle is also known once for all. To use the picnometer, it is simply filled with the liquid to be ex-

amined and weighed. The weight obtained, minus that of the bottle, is the specific gravity sought if the bottle contain 1000 c.c.; $\frac{1}{10}$ if 100 c.c., etc. Example: having a bottle whose weight is 35.35, and which contains 100 c.c.; filled with urine it weighs 137.91, the specific gravity of the urine is 137.91 − 35.35 = 102.56 × 10 = 1025.6 —— Water = 1000.

Second.—The method by the hydrometer is based upon the fact that a solid will sink in a liquid until it has displaced a volume of the liquid whose weight is equal to its own; and all forms of hydrometers are simply contrivances to measure the volume of liquid which they displace when immersed. The appearance of the hydrometer most used by physicians, the urinometer, is too well known to require description. It should not be chosen too small, as the larger the bulb and the thinner and longer the stem, the more accurate will be its indications. Owing to prevailing carelessness in the manufacture of urinometers and to the impossibility of reading the graduations with the same accuracy that can be attained in detecting small differences in weight, their indications are never as precise as those obtained by the picnometer.

In all determinations of specific gravity it is of great importance to have the liquid examined at the temperature for which the instrument is graduated, for the reason that all liquids expand with heat and contract when cooled, and consequently the result obtained will be too low if the urine or other liquid be at a temperature above that at which the instrument is intended to be used, and too high if below that temperature. An accurate correction may be made for temperature in simple solutions; in a complex fluid like the urine, however, this can only be done roughly by allowing 1° of specific gravity for each 3° C. (5.4° Fahr.) of variation in temperature.

The determination of the specific gravity of gases and vapors requires all the facilities of a well-appointed laboratory, and, although of the greatest importance to the chemist (see p. 15), will rarely be attempted by the physician.

States of Matter.—Matter exists in one of three states, solid, liquid, and gaseous. In the solid form the particles of matter are comparatively close together, and are separated with more difficulty than are those of liquid or gaseous matter; or, in other words, the cohesion of solid matter is greater than that of the other two forms. In the liquid the particles are less firmly bound together and are capable of freer motion about one another. In the gas the mutual attraction of the particles disappears entirely, and their distance from each other depends upon the pressure to which the gas is subjected.

The term *fluid* applies to both liquids and gases, the former being designated as *incompressible*, from the very slight degree to which their volume can be reduced by pressure. The gases are designated as *compressible fluids*, from the fact that their volume can be reduced by pressure to an extent limited only by their passage into the liquid form.

It is highly probable that all substances which are not decomposed when heated are capable of existing in the three forms of solid, liquid, and gas. There are, however, some substances which are only known in two forms—as alcohol, or in a single form—as carbon; probably because we are as yet unable to produce artificially a temperature sufficiently low to solidify the one, or sufficiently high to liquefy or volatilize the other.

The passage of a substance from one form to another is always attended by the absorption or liberation of a definite amount of heat. In passing from the solid to the gaseous form a body absorbs a definite

amount of heat with each change of form. If a given quantity of ice at a temperature below the freezing-point of water be heated, its temperature gradually rises until the thermometer marks 0° C., at which point it remains stationary until the last particle of ice has disappeared. At that time another rise of the thermometer begins, and continues until 100° C. is reached (at 760 mm. of barometric pressure), when the water boils, and the thermometer remains stationary until the last particle of water has been converted into steam; after which, if the application of heat be continued, the thermometer again rises. During these two periods of stationary thermometer, heat is taken up by the substance, but is not indicated by the thermometer or by the sense. Not being sensible, it is said to be *latent*, a term which is liable to mislead, as conveying the idea that heat is stored up in the substance *as heat;* such is not the case. During the period of stationary thermometer the heat is not sensible as heat, for the reason that it is being used up in the *work* required to effect that separation of the particles of matter which constitutes its passage from solid to liquid or from liquid to gas. The amount of heat required to bring about the passage of a given weight of a substance from the denser to the rarer form is always the same, and the *temperature* indicated by the thermometer during this passage is always the same for that substance, unless in either case a modification be caused by a variation in pressure. The degree of temperature indicated by the thermometer while a substance is passing from the solid to the liquid state is called its *fusing-point;* that indicated during its passage from the liquid to the gaseous form, its *boiling-point.*

The absorption of heat by a volatilizing liquid is utilized in the arts and in medicine for the production of cold (which is simply the absence of heat), in the manufacture of artificial ice and in the production of local anæsthesia by the ether-spray. The removal of heat from the body in this way, by the evaporation of perspiration from the surface, is an important factor in the maintenance of the body temperature at a point consistent with life.

When a substance passes from a rarer to a denser form it gives out—liberates—an amount of heat equal to that which it absorbed in its passage in the opposite direction. It is for this reason that, while we apply heat to convert a liquid into a vapor, we apply cold to reduce a gas to a liquid. As a rule, the thermometrical indication is the same in whichever direction the change of form occurs; some substances, however, solidify at a temperature slightly different from that at which they fuse.

Most solids, when heated, are first converted into liquids, and these into gases; there are, however, some exceptions to this rule. Solids which pass directly from the solid to the gaseous form are said to *sublime.*

Divisibility.—All substances are capable of being separated, with greater or less facility, by mechanical means into minute particles. With suitable apparatus, gold may be divided into fragments, visible by the aid of the microscope, whose weight would be $\frac{1}{5000000000}$ of a grain; and it is probable that when a solid is dissolved in a liquid a still greater subdivision is attained.

Although we have no direct experimental evidence of the existence of a limit to this divisibility, we are warranted in believing that matter is not infinitely divisible. A strong argument in favor of this view being that, after physical subdivision has reached the limit of its power with regard to compound substances, these may be further divided into dissimilar bodies by chemical means.

The limit of mechanical subdivision is the *molecule* of the physicist, the smallest quantity of matter with which he has to deal.

Elements and Compounds.

If we examine the various substances existing upon and in our earth, we find that many of them can be so decomposed as to yield two or more other substances, distinct in their properties from the substance from whose decomposition they resulted, and from each other. If, for example, sugar be treated with sulphuric acid it blackens, and after a while a mass of charcoal separates. Upon further examination we find that water has also been produced. From this water we may by simple means obtain two gases, differing from each other widely in their properties. Sugar is therefor made up of carbon and the two gases, hydrogen and oxygen; but it has the properties of sugar, and not those of either of its constituent parts. Moreover, if we analyze any number of samples of pure sugar, we will find all of them to contain the same proportionate quantities of carbon, hydrogen, and oxygen (see below). Such a substance as sugar is called a *compound.*

There exist in nature other substances which it has been impossible, hitherto, to decompose into other dissimilar bodies; such as those are called *simple substances* or *elements.*

There are *sixty-four* elements at present known; but it is probable that, as our methods of investigation are improved, this number will be increased by the discovery of other elements, existing only in small quantities. Indeed, during the past year or two the discovery of elements not included in the above number, *scandium*, *decipium*, *philippium*, and of *ytterbium*, has been announced.

Laws Governing the Combination of Elements.

The alchemists, Arabian and European, contented themselves in accumulating a store of knowledge of isolated phenomena, without, as far as we know, attempting, in any serious way, to group them in such a manner as to learn the laws governing their occurrence. It was not until the latter part of the last century, 1777, that Wenzel, of Dresden, implied, if he did not distinctly enunciate, what is known as the law of reciprocal proportions. A few years later, Richter, of Berlin, confirming the work of Wenzel, added to it the law of definite proportions, usually called Dalton's first law. Finally, as the result of his investigations from 1804 to 1808, Dalton added the law of multiple proportions, and, reviewing the work of his predecessors, enunciated the results clearly and distinctly.

Considering these laws, not in the order of their discovery, but in that of their natural sequence, we have:

The law of definite proportions, stated in modern language, is that *the relative weights of elementary substances in a compound are definite and invariable.* If, for example, we analyze water, we find that it is composed of eight parts by weight of oxygen for each part by weight of hydrogen, and that this proportion exists in every instance, whatever the source of the water. If, instead of decomposing, or *analyzing* water, we start from its elements, and, by *synthesis*, cause them to unite to form water, we find that, if the mixture be made in the proportion of eight oxygen to

one hydrogen by weight, the entire quantity of each gas will be consumed in the formation of water. But if an excess of either have been added to the mixture, that excess will remain after the combination. This is true of all chemical compounds, and in this we have one distinction between a chemical *compound* and a mere *mixture* of two substances; in the former the proportion of the constituents is always the same, while in the latter it is variable. Another distinction between compounds and mixtures is that the former have properties distinct from those of their constituents, and that the properties of these only become evident after decomposition of the compound; while mixtures possess the properties inherent in one or all of their constituents.

The law of multiple proportions, or Dalton's second law, is that *when two elements unite with each other to form more than one compound, the resulting compounds contain simple multiple proportions of one element as compared with a constant quantity of the other.*

Oxygen and nitrogen, for example, unite with each other to form no less than five compounds. Upon analysis we find that in these the two elements bear to each other the following relations by weight:

In the first, 14 parts of nitrogen to 8 of oxygen.
In the second, 14 parts of nitrogen to $8 \times 2 = 16$ of oxygen.
In the third, 14 parts of nitrogen to $8 \times 3 = 24$ of oxygen.
In the fourth, 14 parts of nitrogen to $8 \times 4 = 32$ of oxygen.
In the fifth, 14 parts of nitrogen to $8 \times 5 = 40$ of oxygen.

Finally, the third law, that of *reciprocal proportions*, is to the effect that *the ponderable quantities in which substances unite with the same substance express the relation, or a simple multiple thereof, in which they unite with each other.* Or, as Wenzel stated it, "the weights b, b', b'' of several bases which neutralize the same weight a of an acid are the same which will neutralize a constant weight a' of another acid; and the weights a, $a,'$ $a,''$ of different acids which neutralize the same weight b of a base are the same which will neutralize a constant weight of another base b'."

The Atomic Theory.

The laws of Wenzel, Richter, and Dalton, given above, are simply generalized statements of certain groups of facts, and, as such, not only admit of no doubt, but are the foundations upon which chemistry as an exact science is based. Dalton, seeking an explanation of the reason of being of these facts, was led to adopt the view, held by the Greek philosopher Democritus, that matter was not infinitely divisible. He retained the name *atom* (ἄτομος=indivisible), given by Democritus to the ultimate particles of which matter was supposed by him to be composed; but rendered the idea more precise by ascribing to these atoms real magnitude and a definite weight, and by considering elementary substances as made up of atoms of the same kind, and compounds as consisting of atoms of different kinds.

This hypothesis, the first step toward the atomic theory as entertained to-day, afforded a clear explanation of the numerical results stated in the three laws. If hydrogen and oxygen always unite together in the proportion of one of the former to eight of the latter, it is because, said Dalton, the compound consists of an atom of hydrogen, weighing 1, and an atom

of oxygen, weighing 8. If, again, in the compounds of nitrogen and oxygen, we have the two elements uniting in the proportions 14 : 8——14: 8×2——14 : 8×3——14 : 8×4——14 : 8×5, it is because they are severally composed of an atom of nitrogen weighing 14, united to 1, 2, 3, 4 or 5 atoms of oxygen, each weighing 8. Further, that compounds do not exist in which any fraction of 8 oxygen enters, because 8 is the weight of the indivisible atom of oxygen.

One of the chief advantages of Dalton's hypothesis is in the introduction of this precise and simple relation between the quantities of the constituents of a compound. Chemists before Dalton's day, in expressing the results of their analyses, did not progress beyond statements of the percentage composition. Expressing the composition of four of the carbon compounds in percentages, we have:

	Carbon.	Hydrogen.	Oxygen.	
Marsh gas	75.0	25.0	....	=100
Olefiant gas	85.7	14.3	....	=100
Carbonic oxide	42.9	....	57.1	=100
Carbonic acid	27.3	....	72.7	=100

At first sight, these figures convey nothing beyond the mere centesimal composition of the substances which they express. The cardinal point of Dalton's discovery lies in his translation of them into the simple relations:

	Carbon.	Hydrogen.	Oxygen.
Marsh gas	6	2	..
Olefiant gas	6	1	..
Carbonic oxide	6	..	8
Carbonic acid	6	..	16

Dalton's hypothesis of the existence of atoms as definite quantities did not, however, meet with general acceptance. Davy, Wollaston, and others considered the quantities in which Dalton had found the elements to unite with each other, as mere *proportional numbers*, or *equivalents*, as they expressed it, nor is it probable that Dalton's views would have received any further recognition until such time as they might have been exhumed from some musty tome, had their publication not been closely followed by that of the results of the labors of Humboldt and of Gay Lussac, concerning the *volumes* in which gases unite with each other.

In the form of what are known as Gay Lussac's laws, these results are:

First.—There exists a simple relation between the volumes of gases which combine with each other.

Second.—There exists a simple relation between the sum of the volumes of the constituent gases, and the volume of the gas formed by their union. For example:

1 volume chlorine unites with 1 volume hydrogen to form 2 volumes hydrochloric acid.

1 volume oxygen unites with 2 volumes hydrogen to form 2 volumes vapor of water.

1 volume nitrogen unites with 3 volumes hydrogen to form 2 volumes ammonia.

1 volume oxygen unites with 1 volume nitrogen to form 2 volumes nitric oxide.
1 volume oxygen unites with 2 volumes nitrogen to form 2 volumes nitrous oxide.

Berzelius, basing his views upon these results of Gay Lussac, modified the hypothesis of Dalton and established a distinction between the *equivalents* and *atoms*. The composition of water he expressed, in the notation which he was then introducing, as being H_2O, and not HO as Dalton's hypothesis called for. As, however, Berzelius still considered the atom of oxygen as weighing 8, he was obliged also to consider the atoms of hydrogen and of certain other elements as double atoms—a fatal defect in his system, which led to its overthrow and the re-establishment of the formula HO for water.

It was reserved to Gerhardt to clearly establish the distinction between atom and molecule; to observe the bearing of the discoveries of Avogadro and Ampère upon chemical philosophy; and thus to establish the atomic theory as entertained at present.

As a result of his investigations in the domain of organic chemistry, Gerhardt found that, if Dalton's equivalents be adhered to, whenever carbonic acid or water is liberated by the decomposition of an organic substance, it is invariably in double equivalents, never in single ones; always $2CO_2$ or 2HO or some multiple thereof, never CO_2 or HO. He further found that if the equivalents C=6, H=1, and O=8 be retained, the formulæ became such that the equivalents of carbon are always divisible by two. In fact, he found the same objections to apply to the notation then in use, that had been urged against that of Berzelius.

In 1811, Avogadro, from purely physical researches, had been enabled to state the law which is now known by his name, to the effect that *equal volumes of all gases, under like conditions of temperature and pressure, contain equal numbers of molecules.*

In the hands of Gerhardt this law, in connection with those of Gay Lussac, became the foundation of what is sometimes called the "new chemistry." Bearing in mind Avogadro's law, we may translate the first three combinations given in the table on p. 9 into the following:

1 molecule of chlorine unites with 1 molecule of hydrogen to form 2 molecules of hydrochloric acid.
1 molecule of oxygen unites with 2 molecules of hydrogen to form 2 molecules of vapor of water.
1 molecule of nitrogen unites with 3 molecules of hydrogen to form 2 molecules of ammonia.

But the ponderable quantities in which these combinations take place are:

35.5 chlorine to..... 1 hydrogen.
16 oxygen to..... 2 hydrogen.
14 nitrogen to..... 3 hydrogen.

And as single molecules of hydrogen, oxygen, and nitrogen are in these combinations subdivided to form 2 molecules of hydrochloric acid, water, and ammonia, it follows that these molecules must each contain two equal quantities of hydrogen, oxygen, and nitrogen, less in size than the molecules themselves. And, further, as in these instances each molecule

contains two of these smaller quantities, or *atoms*, the relation between the weights of the molecules must be also the relation between the weights of the atoms, and we may therefor express the combinations thus:

1 atom of chlorine weighing 35.5	unites with	1 atom of hydrogen weighing 1;
1 atom of oxygen weighing 16	unites with	2 atoms of hydrogen weighing 1 each;
1 atom of nitrogen weighing 14	unites with	3 atoms of hydrogen weighing 1 each;

and consequently, if the atom of hydrogen weighs 1, that of chlorine weighs 35.5, that of oxygen 16, and that of nitrogen 14.

Atomic and Molecular Weights—Valence.

Atomic weights.—The distinction between molecules and atoms may be expressed by the following definitions:

A molecule is the smallest quantity of any substance that can exist in the free state.

An atom is the smallest quantity of an elementary substance that can enter into a chemical reaction.

The molecule is always made up of atoms, upon whose nature, number, and arrangement with regard to each other, the properties of the substance depend. In an elementary substance the atoms composing the molecules are the same in kind, and usually two in number. In compound substances they are dissimilar and vary in quantity from two in a simple compound, like hydrochloric acid, to several hundreds in the more complex organic substances. Obviously, the word *atom* can only be used in speaking of an elementary body, and that only while it is passing through a reaction. The term *molecule*, on the other hand, applies indifferently to elements and compounds.

The atoms have, as we have seen, definite relative weights; and upon an exact determination of these weights depends the entire science of quantitative analytical chemistry. A vast amount of labor has been bestowed upon fixing these quantities accurately. Berzelius, who was the first to recognize their importance, devoted over thirty years to the task, which he performed so carefully that many of the weights which he gave are those still in use. Subsequently, as new elements were discovered, and as methods of investigation were improved, other determinations were made by Dumas, Marignac, Erdmann, Marchand, Stas, Cooke, and others.

These weights, determined by repeated and careful analyses of perfectly pure compounds of the elements, express the weight of one atom of the element as compared with the weight of one atom of hydrogen, that being the lightest element known. What the *absolute weight* of an atom of any element may be we do not know, nor would the knowledge be of any service did we possess it.

The following table contains a list of the elements at present known, with their atomic weights:

ELEMENTS.

Name.	A. Symbol.	B. Atomic weight.	C. Specific heat.	D. Atomic heat. B × C.
Aluminium	Al.	27.5	0.2143	5.89
Antimony	Sb.	120	0.05077	6.09
Arsenic	As.	75	0.08140	6.10
Barium	Ba.	137.2	....	....
Bismuth	Bi.	210	0.03084	6.48
Boron	Bo.	11	0.3663	3.99
Bromine	Br.	79.952	0.08432	6.74
Cadmium	Cd.	112	0.05669	6.35
Cæsium	Cs.	132.6	....	....
Calcium	Ca.	40	0.17	6.80
Carbon	C.	12	0.4589	5.51
Cerium	Ce.	138	0.04479	6.18
Chlorine	Cl.	35.457	0.093	3.30
Chromium	Cr.	52.4	....	....
Cobalt	Co.	59	0.10696	6.31
Copper	Cu.	63.5	0.09515	6.04
Didymium	D.	144.78	0.04563	6.60
Erbium	E.	162	....	....
Fluorine	Fl.	19	....	....
Gallium	Ga.	69.9	0.0802	5.61
Glucinum	Gl.	13.8	0.4079	5.63
Gold	Au.	197	0.03244	6.39
Hydrogen	H.	1	2.41	2.41
Indium	In.	113.4	0.057	6.46
Iodine	I.	126.85	0.05412	6.87
Iridium	Ir.	197.2	0.03259	6.43
Iron	Fe.	56	0.11379	6.37
Lanthanium	La.	139	0.04485	6.23
Lead	Pb.	206.92	0.03140	6.50
Lithium	Li.	7	0.9408	6.58
Magnesium	Mg.	24	0.2499	6.00
Manganese	Mn.	55.2	0.1217	6.72
Mercury	Hg.	200	0.03332	6.66
Molybdenum	Mo.	96	0.07218	6.93
Nickel	Ni.	59	0.10863	6.41
Niobium	Nb.	94	....	....
Nitrogen	N.	14.044	0.1652	2.32
Osmium	Os.	200	0.03113	6.23
Oxygen	O.	16	0.145	2.32
Palladium	Pd.	106.5	0.0593	6.32
Phosphorus	P.	31	0.1887	5.85
Platinum	Pt.	198	0.03244	6.42
Potassium	K.	39.137	0.1655	6.48
Rhodium	Rh.	104	0.05803	6.04
Rubidium	Rb.	85.4	....	....
Ruthenium	Ru.	104	....	....

ELEMENTS—*Continued.*

Name.	A. Symbol.	B. Atomic weight.	C. Specific heat.	D. Atomic heat. B × C.
Selenium	Se.	79	0.08468	6.69
Silicon	Si.	28	0.2029	5.68
Silver	Ag.	107.93	0.05701	6.15
Sodium	Na.	23.043	0.2934	6.76
Strontium	Sr.	87.5	....	....
Sulphur	S.	32.075	0.20259	6.50
Tantalum	Ta.	137.6	....	....
Tellurium	Te.	128	0.05155	6.59
Thallium	Tl.	204	0.03355	6.84
Thorium	Th.	234	....	....
Tin	Sn.	118	0.05623	6.63
Titanium	Ti.	50	....	....
Tungsten	W.	184	0.03342	6.15
Uranium	U.	120	....	....
Vanadium	V.	51.3	....	....
Yttrium	Y.	92.5	....	....
Zinc	Zn.	65.2	0.09555	6.23
Zirconium	Zr.	89.6	0.0666	5.97

We are not limited to chemical means in fixing atomic weights; indeed, cases frequently arise in which the results of numerous analyses are such as would agree with one or more numbers equally well. In these cases we obtain valuable indications from the physical properties of the substances whose atomic weights are not clearly definable by chemical means.

A most valuable aid in this respect is the law of Dulong and Petit. These observers found, in 1819, that there existed a definite relation between the atomic weight of an element and its specific heat (see p. 30), and that the product obtained by multiplying these two quantities together was, with a few exceptions, nearly constant. While the atomic weights differ greatly from each other—7 and 234 being the extremes—the specific heats differ in an opposite manner, and to such an extent that the product obtained by multiplying the two together does not vary much from 6.4. This product is given for each element in the above table as its *atomic heat.*

If by analytical means we are unable to determine which of two numbers is the correct atomic weight of an element, we determine its specific heat and select that one of the two numbers under consideration which, when multiplied by the specific heat, gives a result most nearly approaching 6.4.

It will be noticed, on examining the table, that the atomic heats of certain of the elements vary considerably from the rule. The atomic heats of carbon, boron, silicon, sulphur, and phosphorus are subject to great variations, as will be seen in the following table:

		Specific heat.	Atomic heat.
Boron.			
Crystallized	at— 39.6°	0.1915	2.11
Crystallized	at+ 76.7°	0.2737	3.01
Crystallized	at+233.2°	0.3663	3.99
Amorphous		0.255	2.81
Carbon.			
Diamond	at— 50.5°	0.0635	0.76
Diamond	at+140°	0.2218	2.66
Diamond	at+985°	0.4589	5.51
Graphite	at— 50.3°	0.1138	1.37
Graphite	at+138.5°	0.2542	3.05
Graphite	at+977.9°	0.4670	5.60
Wood charcoal		0.2415	2.90
Silicon.			
Crystallized	at— 39.8°	0.1360	3.81
Crystallized	at+128.7°	0.1964	5.50
Crystallized	at+232.4°	0.2029	5.68
Fused	at+100°	0.175	4.90
Sulphur.			
Orthorhombic	at+ 45°	0.163	5.22
Orthorhombic	at+ 99°	0.1776	5.68
Liquid	at+150°	0.234	7.49
Recently fused	at+ 98°	0.20259	6.48
Phosphorus.			
Yellow	at— 78°	0.174	5.39
Yellow	at+ 36°	0.202	6.26
Liquid	at+100°	0.212	6.57
Amorphous	at+ 98°	0.170	5.27

It will be observed that, as the temperature of the *solid* element is increased, the atomic heat more nearly approaches 6.4. It will further be noticed that those elements with which the perturbations occur are precisely those which are capable of existing in two or more allotropic forms (see p. 30). As in the passage of an element from one allotropic condition to another, absorption or liberation of heat always takes place, as the result of "interior work;" it is more than probable that these perturbations are due to a constant tendency of the element to pass from one allotropic condition to another.

The atomic heats of those elementary gases which have only been liquefied by enormous cold and pressure are tolerably constant at about 2.4.

Other considerations of a physical nature having a bearing upon the atomic weights will be considered later.

Molecular weight.—The molecular weight of a substance is the weight of its molecule as compared with the weight of an atom of hydrogen. It is also, obviously, the sum of the weights of all the atoms making up the molecule.

The determination of molecular weight is chiefly of importance in the study of the compounds of carbon. We can readily determine the percentage composition of an organic body by analysis; this does not, however, indicate the number of atoms of each of the constituent ele-

ments. For example, if we analyze the gas acetylene, and the liquid benzene, we obtain the following results:

	Acetylene.	Benzene.	
Carbon	92.31	92.31	24
Hydrogen	7.69	7.69	2
	100.00	100.00	26

Upon further examination we find the molecular weight of acetylene to be 26, and consequently we know its molecule to consist of two atoms of carbon and two of hydrogen. The molecular weight of benzene, on the other hand, being 78, or 26×3, we know that its molecule consists of six atoms each of carbon and hydrogen.

A very ready means of determining the molecular weight of any substance which we can convert into a gas is based upon Avogadro's law. The specific gravity of a gas is the weight of a given volume as compared with that of an equal volume of hydrogen. But these equal volumes contain equal numbers of molecules (p. 10), and therefor, in determining the specific gravity of a gas, we obtain the weight of its molecule as compared to that of a molecule of hydrogen; and, as the molecule contains two atoms of hydrogen, while one atom of hydrogen is the unit of comparison, it follows that the specific gravity of a gas, multiplied by two, is its molecular weight.

VALENCE, OR ATOMICITY.

By the *valence* of an element is understood the combining capacity of its atoms. We know that

One atom of chlorine combines with one atom of hydrogen,
One atom of oxygen combines with two atoms of hydrogen,
One atom of nitrogen combines with three atoms of hydrogen,
One atom of carbon combines with four atoms of hydrogen,

and that the atoms of different elements thus possess different powers of holding hydrogen in combination. In the compounds formed by the above unions chlorine is *univalent*, oxygen is *divalent*, nitrogen is *trivalent*, and carbon is *quadrivalent*.

But the valence of the elements is not fixed and invariable. Thus, while chlorine and iodine each combine with hydrogen, atom for atom, and in those compounds are consequently univalent, they unite with each other to form two compounds—one containing one atom of iodine and one of chlorine, the other containing one atom of iodine and three of chlorine; chlorine being univalent, iodine is obviously trivalent in the second of these compounds. Again, phosphorus forms two chlorides, one containing three, the other five atoms of chlorine, to one of phosphorus.

In view of these facts, we must consider, either: 1, that the valence of an element is that which it exhibits in its most saturated compounds, as phosphorus in the pentachloride, and that the lower compounds are nonsaturated and have free valences; or 2, that the valence is variable. The first supposition depends too much upon the chances of discovery of compounds in which the element has a higher valence than that which might

be considered as the maximum to-day. The second supposition—notwithstanding the fact that, if we admit the possibility of two distinct valences, we must also admit the possibility of others—is certainly the more tenable and the more natural. In speaking, therefor, of the valence of an element, we must not consider it as an absolute quality of its atoms, but simply as their combining power in the particular class of compounds under consideration. Indeed, compounds are known in whose molecules the atoms of one element exhibit two distinct valences; thus, ammonium cyanate contains two atoms of nitrogen: one in the ammonium group is quinquivalent, one in the acid radical is trivalent.

It has been found that, in the great majority of instances in which an element exhibits different valences, they differ from each other by two. Thus, phosphorus is trivalent or quinquivalent; platinum is divalent or quadrivalent.

The valence of an atom is expressed in notation by signs placed above and to the right of the symbol (see below), thus: Cl', univalent; O'', divalent; N''', trivalent; C^{iv}, quadrivalent; P^{v}, quinquivalent; $(Fe_2)^{vi}$, hexavalent.

Symbols—Formulæ—Equations.

Symbols.—These are conventional abbreviations of the names of the elements, whose purpose it is to introduce simplicity and exactness into descriptions of chemical actions. They consist of the initial letter of the Latin name of the element, to which is usually added one of the other letters. If there be more than two elements whose names begin with the same letter, the single-letter symbol is reserved for the commonest element. Thus, we have nine elements whose names begin with C; of these the commonest is Carbon, whose symbol is C; the others have double-letter symbols, as Chlorine, Cl; Cobalt, Co; Copper, Cu (Cuprum), etc.

These symbols do not indicate simply an indeterminate quantity, but *one atom* of the corresponding element. When more than one atom is spoken of, the symbol is not repeated, but the number of atoms which it is desired to indicate is written either before the symbol, or, in small figures, after and below it; thus, H indicates one atom of hydrogen; 2Cl, two atoms of chlorine; C_4, four atoms of carbon, etc.

Formulæ.—What the symbol is to the element, the formula is to the compound; by it the number and kind of atoms of which the molecule of a substance is made up are indicated. The simplest kind of formulæ are what are known as *empirical formulæ;* which indicate only the kind and number of atoms which form the compound. Thus, HCl indicates a molecule composed of one atom of hydrogen united with one atom of chlorine; $5H_2O$, five molecules, each composed of two atoms of hydrogen and one atom of oxygen, the number of molecules being indicated by the proper numeral placed before the formula, in which place it applies to all the symbols following it. Sometimes it is desired that a numeral shall apply to a part of the following symbols only, in which case they are enclosed in parentheses, thus: $3(SO_4)Al_2$, means 3 times SO_4 and twice Al. This may also be written $(SO_4)_3Al_2$.

For the other varieties of formulæ, see p. 23.

Equations are combinations of formulæ and algebraic signs so arranged as to indicate a chemical reaction and its results. The signs used are the plus and equality signs; the former being equivalent to "and," and the second meaning "have reacted upon each other and have produced." The

substances entering into the reaction are placed before the equality sign and the products of the reaction after it; thus, the equation

$$2KHO+SO_4H_2=SO_4K_2+2H_2O$$

means, when translated into ordinary language: two molecules of potash, each composed of an atom of potassium, one atom of hydrogen and one atom of oxygen, *and* one molecule of sulphuric acid, composed of one atom of sulphur, four atoms of oxygen and two atoms of hydrogen, *have reacted upon each other and have produced* one molecule of potassium sulphate, composed of one atom of sulphur, four atoms of oxygen and two atoms of potassium, *and* two molecules of water, each composed of two atoms of hydrogen and one atom of oxygen. The saving of time and labor by the use of symbols is obvious from this example. As no material is ever lost or created in a reaction, the number of each kind of atom occurring before the equality sign in an equation must always be the same as that occurring after it.

Radicals—Acids—Bases and Salts.

Radicals.—In the molecules of compound substances the atoms are not placed at random, but certain of them are attached more closely to each other than they are to the remainder; and most, if not all, compounds contain within the molecule a group of atoms, whose valences are not all satisfied, and in which the atoms are so closely linked that the entire group is capable of passing readily from one combination to another unchanged, although it is not necessarily capable of a separate existence; such a group is called a *radical.* Marsh-gas, for instance, has the empirical formula CH_4. By acting upon this substance in suitable ways, we can cause the atom of carbon, accompanied by three of the hydrogen atoms, to pass unchanged into a variety of other substances, such as: $(CH_3)Cl$; $(CH_3)OH$; $(CH_3)_2O$; $C_2H_2O_2$ (CH_3), etc.; we therefor consider marsh-gas as made up of the radical (CH_3) combined with an atom of hydrogen, $(CH_3)H$. It is usual to enclose the radical in brackets or parentheses to indicate its nature.

Like the elements, the radicals possess different valences, depending upon the number of unsatisfied elementary valences which they contain. Thus, in the radical (CH_3) three of the four valences of the atom of carbon are satisfied by three atoms of hydrogen; the remaining free valence of the carbon atom renders the radical univalent; it gives it a power of combination equal to that of an atom of a univalent element. These radicals play an important part in the chemistry of the carbon compounds.

Acids.—It is a difficult matter to give a concise definition of an acid, which shall cover the meaning fully. The usual definition is "a compound of an electro-negative radical with hydrogen, which hydrogen it can part with in exchange for a metal or basylous radical," which is probably as satisfactory a definition as can be given at present. The two characteristics of an acid being that it contains, on the one hand, an electro-negative radical or element, and, on the other hand, hydrogen capable of being replaced by an electro-positive radical or element. The atoms of hydrogen so replaceable are termed the *basic* or *replaceable hydrogen* of the acid, the acid itself being designated as *monobasic, dibasic, tribasic, tetrabasic,* etc., according as it contains one, two, three, four, etc., atoms of such replaceable hydrogen.

By *electro-positive* or *basylous* elements or radicals are meant such as are disengaged at the zinc or negative pole, when their compounds are decomposed by the action of the galvanic battery.

By *electro-negative* or *acidulous* are meant such as are disengaged at the platinum or positive pole under like circumstances. In the following table are given the electric conditions of the more important elements and radicals:

Electro-positive, or Basylous.		Electro-negative, or Acidulous.	
Hydrogen.	Copper.	Oxygen.	Arsenic.
Potassium.	Mercury.	Fluorine.	Antimony.
Sodium.	Tin.	Chlorine.	Boron.
Lithium.	Iron.	Bromine.	Carbon.
Silver.	Cobalt.	Iodine.	Silicium.
Ammonium.	Nickel.	Sulphur.	Molybdenum.
Calcium.	Gold.	Selenium.	Tungsten,
Barium.	Bismuth.	Tellurium.	and their oxidized
Zinc.	Platinum.	Nitrogen.	radicals.
Magnesium.	Aluminium.	Phosphorus.	Cyanogen.
Cadmium.	Chromium.		
Lead.	Alcoholic radicals.		

Bases.—A base is a compound of hydrogen and oxygen with an electro-positive element or radical, which it is capable of giving up in exchange for the hydrogen of an acid; indeed, it may be considered as one or more molecules of water, in which one-half the hydrogen has been replaced by an electro-positive element or radical. Thus, KHO, potassium hydrate; $(NH_4)HO$, ammonium hydrate. These substances, being considered as derived from water, are called *hydrates;* they are, according to existing views, the only substances to which the term *base* properly applies.

Bases and acids are capable of what is called *double decomposition* with each other. That is, the acid and base are both decomposed, while water and a salt are formed:

$$KHO + NO_2H = H_2O + NO_2K.$$

Potassium hydrate. Nitric acid. Water. Potassium nitrate.

Salts are substances formed by the substitution of basylous radicals or elements for a part or all of the replaceable hydrogen of an acid. They are always formed, therefor, when bases and acids enter into double decomposition. They are not, as was formerly supposed, formed by the union of a metallic with a non-metallic oxide, but, as stated above, by the substitution of one or more atoms of an element or radical for the hydrogen of the acid. Thus, the compound formed by the action of sulphuric acid upon quicklime is not SO_2CaO, but SO_4Ca, formed by the interchange of atoms

$$\begin{matrix} S \\ O_4 \longrightarrow \\ H_2) \longrightarrow \end{matrix} \quad \begin{matrix} \\ \longleftarrow (Ca \\ \longrightarrow O \end{matrix}$$

and not

$$\begin{matrix} S \\ O_2 \longrightarrow \\ \end{matrix} \quad \begin{matrix} \\ \longleftarrow (Ca \\ O \end{matrix}$$

$$\longleftarrow (H_2 \\ O$$

for which reason it is not the sulphate of *lime*, as it was formerly called, but *calcium sulphate.*

The basylous element of a salt is endowed with considerable mobility, and may be readily transferred from one acid radical to another; or liberated by the presence of an acid radical with which it has a greater tendency to unite (for which it has a greater affinity), or of an element whose tendency to unite with its acidulous radical is greater than its own. Thus, if sodium sulphate and barium nitrate be brought together in solution, the following double decomposition occurs:

$$SO_4Na_2+(NO_3)_2Ba=SO_4Ba+2NO_3Na.$$

Again, silver is separated from the nitrate by the presence of mercury; lead from its acetate in the presence of zinc; copper from its sulphate in the presence of iron, etc.

If two acids be brought in the presence of a single base, the latter is divided by the former according to their affinities, subject to the modifications due to the volatility of the acid, or its insolubility, or the insolubility of the salt formed.

If one of the acids be volatile at the temperature at which the reaction occurs, it is driven off. Sodium nitrate and sulphuric acid may exist together at ordinary temperatures, but upon heating the mixture the nitric acid is driven off and sodium sulphate is formed.

If one of the acids be insoluble, its influence becomes nil—it separates in the solid form while the other takes its place; thus, if potassium silicate and hydrochloric acid be brought together, potassium chloride remains in the solution and silicic acid separates.

Whenever two salts in solution are brought together, the basylous element of one of which is capable of uniting with the acidulous radical of the other to form an *insoluble salt*, the insoluble compound is formed. Thus, if a solution of a sulphate be added to a solution of a barium salt, the insoluble barium sulphate is precipitated.

What has been stated of two acids in presence of one base also applies to two bases in presence of one acid.

The term *salt*, as used at present, applies to the compound formed by the substitution of another element for the hydrogen of *any* acid; and indeed, as used by some authors, to the acids themselves, which are considered as salts of hydrogen. It is probable, however, that eventually the name will be limited to such compounds as correspond to acids whose molecules contain more than two elements. Indeed, from the earliest times of modern chemistry, a distinction was observed between the *haloid salts, i. e.*, those the molecules of whose corresponding acids consisted of hydrogen united with one other element, on the one hand; and the salts of the oxacids, *i. e.*, those into whose composition oxygen entered, on the other hand. This distinction, however, has gradually fallen into the background, for the reason that the methods and conditions of formation of the two kinds of salts are usually the same *when the basylous element belongs to that class of elements usually designated as metallic.*

There are, nevertheless, important distinctions between the two kinds of salts, which we believe to be of sufficient importance not only to mention, but to make a factor in the classification of the elements (see p. 26). The salts of the hydracids (haloid salts) may be readily obtained without the previous formation of the acid, as potassium unites directly with chlorine to form potassium chloride. The salts of the oxacids, on the

other hand, are only formed by the substitution of the basylous element for the hydrogen of the previously formed acid, by some double decomposition or by the oxidation of an existing compound, in all cases in which the corresponding acid is capable of separate existence. There are, for example, three methods of formation of potassium sulphate: either by the action of the basylous element or its hydrate upon sulphuric acid—

$$SO_4H_2+K_2 = SO_4K_2+H_2$$
$$SO_4H_2+2KHO=SO_4K_2+2H_2O;$$

or by double decomposition—

$$2NO_3K+SO_4H_2=SO_4K_2+2NO_3H;$$

or by the oxidation of the sulphide—

$$SK_2+2O_2=SO_4K_2.$$

In those cases in which the acid corresponding to the salt has not been obtained, it is more than probable that the formation of the acid precedes that of the salt. The true carbonic acid, for instance, CO_3H_2, is not known, yet its anhydride, CO_2, is capable of forming salts; but, as the formation of these salts occurs only in the presence of water, we may infer that the reaction

$$CO_2+H_2O=CO_3H_2$$

occurs before the formation of the salt.

An important difference between the two classes of compounds, and one which we have utilized in our classification of the elements, is that, while there exist compounds of all the elements corresponding to the hydracids, there are many elements which are not capable of replacing the hydrogen of the oxacids to form salts; and those elements, thus incapable of forming oxysalts, are strongly electro-negative, and their oxides are capable of uniting with water to form acids (see p. 27).

Nomenclature.

The names of the elements are mostly of Greek derivation, and have their origin in some prominent property of the substance; thus, *phosphorus*, *φῶς*, light, and *φέρειν*, to bear. Some are of Latin origin, as *silicon*, from *silex*, flint; some of Gothic origin, as *iron*, from *iarn;* and others are derived from modern languages, as *potassium*, from *pot-ash*. Very little system has been followed in naming the elements, beyond applying the termination *ium* to the metals, and *ine* or *on* to the metalloids; and even to this rule we find such exceptions as a metal called *manganese* and a metalloid called *sulphur*.

The names of *compound substances* were formerly chosen upon the same system, or rather lack of system, as those of the elements. So long as the number of compounds with which the chemist had to deal remained small, the use of these fanciful appellations, conveying no more to the mind than perhaps some unimportant quality of the substances to which they applied, gave rise to comparatively little inconvenience. In these later days, however, when the number of compounds has risen high in the thousands, some systematic method has become absolutely necessary.

The principle at the base of the system of nomenclature at present used is that the name shall itself convey, as far as possible, the composition and character of the substance.

Compounds consisting of two elements, or of an element and a radical only, *binary compounds*, are designated by compound names made up of the name of the more electro-positive, followed by that of the more electro-negative, in which the termination *ide* has been substituted for the terminations *ine*, *on*, *ogen*, *ygen*, *orus*, *ium*, and *ur*. For example: the compound of potassium and chlorine is called potassium chlor*ide*, that of potassium and oxygen, potassium ox*ide*, that of potassium and phosphorus, potassium phosph*ide*.

In a few instances the older name of a compound is used in preference to the one which it should have under the above rule, for the reason that the substance is one which is typical of a number of other substances, and therefor deserving of exceptional prominence; such are *ammonia*, NH_3; *water*, H_2O.

When, as frequently happens, two elements unite with each to form more than one compound, these are usually distinguished from each other by prefixing to the last word of the name the Greek numeral corresponding to the number of atoms of the element designated by that word, as compared with a *fixed* number of atoms of the other element.

Thus, in the series of compounds of nitrogen and oxygen, most of which contain two atoms of nitrogen, N_2 is the standard of comparison, and consequently the names are as follows:

N_2O = Nitrogen *mon*oxide.
NO ($=N_2O_2$) = Nitrogen *di*oxide.
N_2O_3 = Nitrogen *tri*oxide.
N_2O ($=N_2O_4$) = Nitrogen *tetr*oxide.
N_2O_5 = Nitrogen *pent*oxide.

Another method of distinguishing two compounds of the same two elements consists in terminating the first word in *ous* in that compound which contains the less proportionate quantity of the more electro-negative element, and in *ic* in that containing the greater proportion; thus:

SO_2 = Sulphur*ous* oxide.
SO_3 = Sulphur*ic* oxide.

Hg_2Cl_2 (2Hg : 2Cl) = Mercur*ous* chloride.
$HgCl_2$ (2Hg : 4Cl) = Mercur*ic* chloride.

This method, although used to a certain extent in speaking of compounds composed of two elements of Class II. (see p. 27), is used chiefly in speaking of binary compounds of elements of different classes.

In naming the *oxacids* the word *acid* is used, preceded by the name of the electro-negative element other than oxygen, to which a prefix or suffix is added to indicate the degree of oxidation. If there be only two, the least oxidized is designated by the suffix *ous*, and the more oxidized by the suffix *ic*, thus:

NO_2H = Nitr*ous* acid.
NO_3H = Nitr*ic* acid.

If there be more than two acids, formed in regular series, the least oxi-

dized is designated by the prefix *hypo* and the suffix *ous;* the next by the suffix *ous;* the next by the suffix *ic;* and the most highly oxidized by the prefix *per* and the suffix *ic;* thus:

$ClOH$ = *Hypo*chlor*ous* acid.
ClO_2H = Chlor*ous* acid.
ClO_3H = Chlor*ic* acid.
ClO_4H = *Per*chlor*ic* acid.

Certain elements, such as sulphur and phosphorus, exist in acids which are derived from those formed in the regular way, and which are specially designated (see pp. 88, 112).

The names of the salts are derived from those of the acids by dropping the word *acid*, changing the termination of the other word from *ous* into *ite*, or from *ic* into *ate*, and prefixing the name of the electro-positive element or radical; thus:

SO_3H_2 Sulphur*ous* acid.	SO_3K_2 Potassium sulph*ite*.
SO_4H_2 Sulphur*ic* acid.	SO_4K_2 Potassium sulph*ate*.
$ClOH$ Hypochlor*ous* acid.	$ClOK$ Potassium hypochlor*ite*.

Acids whose molecules contain more than one atom of replaceable hydrogen are capable of forming more than one salt with electro-negative elements, or radicals, whose valence is less than their basicity. Ordinary phosphoric acid, for instance, contains in each molecule three atoms of basic hydrogen, and consequently is capable of forming three salts by the replacement of one, two, or three of its hydrogen atoms by one, two, or three atoms of a univalent element; to distinguish these the Greek prefixes *mono, di,* and *tri* are used thus:

PO_4H_2K = *Mono*potassic phosphate.
PO_4HK_2 = *Di*potassic phosphate.
PO_4K_3 = *Tri*potassic phosphate.

The first is also called *dihydro*potassic phosphate, and the second *hydrodi*potassic phosphate.

In the older works, salts in which the hydrogen has not been entirely displaced are sometimes called *bi*salts (bicarbonates), or *acid* salts; those in which the hydrogen has been entirely displaced being designated as *neutral* salts.

A few elements, such as mercury, copper, and iron, form two distinct series of salts; these are distinguished, in the same way as the acids, by the use of the suffix *ous* in the names of those containing the less proportion of electro-negative group and the suffix *ic* in those containing the greater proportion, *e. g.:*

$SO_4(Cu_2)_2$ ..... ($1SO_4$: $4Cu$) = Cupr*ous* sulphate.
SO_4Cu_2 ..... ($2SO_4$: $4Cu$) = Cupr*ic* sulphate.

SO_4Fe ..... ($2SO_4$: $2Fe$) = Ferr*ous* sulphate.
$(SO_4)_3Fe_2$ ..... ($3SO_4$: $2Fe$) = Ferr*ic* sulphate.

The names, *basic* salts, *sub*salts, and *oxy*salts have been applied indifferently to salts, such as the lead subacetates, which are compounds

containing the normal acetate and the hydrate or oxide of lead; and to salts such as the so-called bismuth subnitrate, which is a nitrate, not of bismuth, but of the univalent radical $(Bi'''O'')'$.

By *double salts* are meant such as are formed by the substitution of different elements or radicals for two or more atoms of replaceable hydrogen of the acid, such as ammonio-magnesian phosphate, $PO_4Mg''(NH_4)'$.

Oxides, Hydrates, and Chlorides.

The oxides, hydrates, and chlorides of the various elements differ from each other materially in their properties. The oxides of a certain class of elements, when they unite with water, form hydrates which possess acid properties; such oxides are called *anhydrides*. The oxides of another class of elements unite with water to form hydrates endowed with strongly basic properties. Between these two classes is a third, some of whose oxides form hydrates which are basic in character, while others unite with water to form acids (see p. 27).

As a rule, those elements which form basic hydrates also form chlorides which are either insoluble in water, or soluble without decomposition. Those elements, on the other hand, whose oxides are all anhydrides, form chlorides which are decomposed when they come in contact with water.

Typical Formulæ and Formulæ of Constitution.

The formulæ which we have hitherto used, and which are known as empirical formulæ, indicate only the number and kind of atoms constituting the molecule—indications which would seem at first sight to be all that could be required of them. When, however, it was found that two substances existed, each composed of the same kind and number of atoms, and yet possessing very different physical and chemical properties, the inference naturally followed that these differences must be due to a different arrangement of the atoms within the molecule—a different *constitution*, as it is called. To indicate these differences extended formulæ were devised: *typical formulæ*, which show only the more salient points of the constitution of the substance; and *graphic formulæ*, or *formulæ of constitution*, which are intended to set forth the entire structure of the molecule.

The idea of chemical types was first suggested by Dumas in 1839. In the system of typical formulæ all substances are considered as being so constituted that their rational formulæ may be referred to one of three classes or types, or to a combination of two of these types. These three classes, being named after the most common substance occurring in each, are expressed thus:

The hydrogen type.	The water type.	The ammonia type.
$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$
$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}$	$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2$
etc.,	etc.,	etc.,

it being considered that the formula of any substance of known constitution can be indicated by substituting the proper element, or radical, for one or more of the atoms of the type, thus:

$\left.\begin{matrix}Cl\\H\end{matrix}\right\}$	$\left.\begin{matrix}(C_2H_5)'\\H\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2H_5)'\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}Cl_2\\Ca\end{matrix}\right\}$	$\left.\begin{matrix}(SO_4)''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(CO)''\\H_2\\H_2\end{matrix}\right\}N_2$
Hydrochloric acid.	Alcohol.	Ethylamine.	Calcium chloride.	Sulphuric acid.	Urea.

Typical formulæ are of great service in the classification of compound substances, as well as to indicate, to a certain degree, their nature and the method of the reactions into which they enter.

Referring, for instance, to the formula of marsh-gas, given on p. 17, as $(CH_3)H$, we find that it belongs to the same type as hydrogen, and that its typical formula is $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}$. This formula indicates not only that the substance is composed of the univalent radical CH_3 with an atom of hydrogen, but also that the extra-radical atom of hydrogen, being united to an electro-positive radical, is not replaceable after the manner of the basic hydrogen of an acid, although it may be replaced by an electro-negative element, such as chlorine. The radical CH_3 is also capable of removal and passage into other forms of combination; it may be made to pass from the compound $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}$ into that having the composition $\left.\begin{matrix}CH_3\\Cl\end{matrix}\right\}$, and from that into $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$. The last formula indicates a substance which is of the same type as water, and is consequently the *hydrate* of the radical, a hydrate which, owing to the electro-positive character of the radical, is not acid. If, however, the radical be oxidized, it becomes electro-negative, and the resulting substance, $\left.\begin{matrix}(CHO)'\\H\end{matrix}\right\}O$, is endowed with acid properties, and, as the typical formula indicates, contains a single atom of basic hydrogen.

There are two substances which, on analysis, each prove to have the composition $C_2H_4O_2$, and which, nevertheless, differ from each other widely in their properties. By a further examination of these two substances, we find that one contains the group $(CH_3)'$, while the other contains the group $(C_2H_3O)'$, united to one atom of replaceable hydrogen. The difference in their constitution at once becomes apparent in their typical formulæ, $\left.\begin{matrix}(CHO)'\\(CH_3)'\end{matrix}\right\}O$ and $\left.\begin{matrix}(C_2H_3O)'\\H\end{matrix}\right\}O$, which also indicate differences in their properties, which we find upon experiment to exist. The first substance is neutral in reaction and possesses no acid properties; it closely resembles a salt of an acid having the formula $\left.\begin{matrix}(CHO)\\H\end{matrix}\right\}O$. The second substance, on the other hand, has a strongly acid reaction, and markedly acid properties, as indicated by the oxidized radical and the extra-radical hydrogen. It is capable of forming salts by the substitution of an atom of a univalent basylous element for its single replaceable atom of hydrogen $\left.\begin{matrix}(C_2H_3O)'\\Na\end{matrix}\right\}O$. Again, the action which takes place between caustic potash and acetic acid is indicated more accurately and intelligibly by the typical equation—

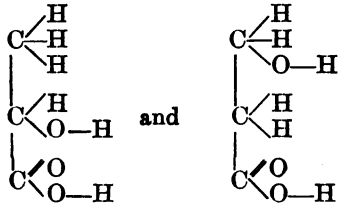
$$\left.\begin{matrix}K\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_2O\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_2O\\K\end{matrix}\right\}O,$$

than by the empirical equation—

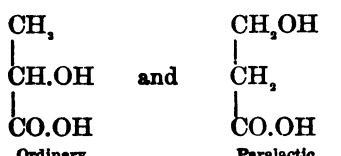
$$KHO + C_2H_4O_2 = H_2O + C_2H_3O_2K.$$

Although typical formulæ have been, and still are, of great service, many cases arise, especially in treating of the more complex organic substances, in which they do not sufficiently indicate the relations between the atoms which constitute the molecule, and thus fail to convey a proper idea of the nature of the substance. Considering, for example, the ordinary lactic acid, we find its composition to be $C_3H_6O_3$, which, expressed typically, would be $\left.\begin{matrix}(C_3H_4O)''\\H_2\end{matrix}\right\}O_2$, a constitution supported by the fact that the radical $(C_3H_4O)''$ may be obtained in other compounds, as $\left.\begin{matrix}(C_3H_4O)''\\Cl_2\end{matrix}\right\}$. This constitution, however, cannot be the true one, because in the first place, lactic acid is not dibasic, but monobasic; and, in the second place, there is another acid, called paralactic acid, having an identical composition, yet differing in its products of decomposition. These differences in the properties of the two acids must be due to a different *arrangement* of atoms in their molecules, a view which is supported by the sources from which they are obtained and the nature of their products of decomposition.

To express the constitution of such bodies, *graphic formulæ* are used, in which the position of each atom in relation to the others is set forth. The constitution of the two lactic acids would be expressed by graphic formulæ in this way:



or,



Ordinary lactic acid. Paralactic acid.

It must be understood that these graphic formulæ are simply intended to show the relative attachments of the atoms, and are in nowise intended to convey the idea that the molecule is spread out upon a flat surface with the atoms arranged as indicated in the diagram. The formula of ordinary lactic acid shows that one of its atoms of carbon has three of its valences satisfied by three atoms of hydrogen, and is attached by its remaining valence to another atom of carbon, one of whose other

valences is satisfied by an atom of hydrogen, another by the univalent group OH, and whose remaining valence attaches it to the third atom of carbon, two of whose remaining valences are satisfied by one atom of the divalent element oxygen, and the last by the group OH.

Great care and much labor are required in the construction of these graphic formulæ, the positions of the atoms being determined by a close study of the methods of formation, and of the products of decomposition of the substance under consideration. Naturally, in a matter of this nature, there is always room for differences of opinion—indeed, the entire atomic theory is open to question, as is the theory of gravitation itself; but, whatever may be advanced, two facts cannot be denied: first, that chemistry owes its advancement within the past half-century to the atomic theory, which to-day is more in consonance with observed facts than any substitute which can be offered; second, that without the use of graphic formulæ it would be impossible to offer any adequate explanation of the reactions which we observe in dealing with the more complex organic substances.

In chemistry, as in other sciences, a sharp distinction must always be made between facts and theory: the former, once observed, are immutable additions to our knowledge; the latter are of their nature subject to change with our increasing knowledge of facts. We have every reason for believing, however, that the supports upon which the atomic theory rests are such that, although it may be modified in its details, its essential features will remain unaltered.

Classification of the Elements.

The necessity of a classification of the elements into groups for convenience of study was felt early in the history of chemistry. Berzelius was the first to divide all the elements into two great classes, to which he gave the names *metals* and *metalloids*. The metals, being such substances as are opaque, possess what is known as metallic lustre, are good conductors of heat and electricity, and are electro-positive; the *metalloids*, on the other hand, such as are gaseous, or, if solid, do not possess metallic lustre, have a comparatively low power of conducting heat and electricity, and are electro-negative.

This division, based, as it will be seen, purely upon physical properties, which, in many cases, are ill-defined, has become insufficient. Several elements formerly classed under the above rules with the metals, such as arsenic and antimony, resemble phosphorus in their chemical characters much more clearly than they do any of the metals; indeed, by the characters mentioned above, it is impossible to draw any line of demarcation which shall separate the elements distinctly into two groups.

The classification of the elements should be such that each group shall contain elements whose *chemical* properties are similar—the *physical* properties being considered only in so far as they are intimately connected with the chemical (see p. 13). The arrangement of elements into groups is not equally easy in all cases; some groups, as the chlorine group, are sharply defined, while the members of others differ from each other more widely in their properties. The positions of most of the more recently discovered elements are still uncertain, owing to the imperfect state of our knowledge of their properties.

The method of classification which we will adopt, and which we believe

to be more natural than any hitherto suggested, is based upon the chemical properties of the oxides and upon the valence of the elements. We would abandon entirely the division into metals and metalloids, and substitute for it a division into four great classes, according to the nature of the oxides and the existence or non-existence of oxysalts. In the first of these classes hydrogen and oxygen are placed together, for the reason that, although they differ from each other in many of their properties, they together form the basis of our classification, and may, for this and other reasons, be regarded as *typical elements*. They both play important parts in the formation of acids, and neither would find a suitable place in either of the other classes. Our primary division would then be as follows:

Class I.—Typical elements.

Class II.—Elements whose oxides unite with water to form acids, never to form bases. Which do not form oxysalts.

This class contains all the so-called metalloids except hydrogen and oxygen.

Class III.—Elements whose oxides unite with water, some to form bases, others to form acids. Which form oxysalts.

Class IV.—Elements whose oxides unite with water to form bases; never to form acids. Which form oxysalts.

In this class are included the more strongly electro-positive metals.

Within the classes a further subdivision is made into groups, each group containing those elements within the class which have equal valences, which form corresponding compounds, and whose *chemical characters* are otherwise similar.

Class I.

GROUP I.—Hydrogen.
GROUP II.—Oxygen.

Class II.

GROUP I.—Fluorine, chlorine, bromine, iodine.
GROUP II.—Sulphur, selenium, tellurium.
GROUP III.—Nitrogen, phosphorus, arsenic, antimony.
GROUP IV.—Boron.
GROUP V.—Carbon, silicon.
GROUP VI.—Vanadium, niobium, tantalium.
GROUP VII.—Molybdenum, tungsten, osmium (?).

Class III.

GROUP I.—Gold.
GROUP II.—Chromium, manganese, iron.
GROUP III.—Aluminium, gallium (?), indium (?), glucinium.
GROUP IV.—Uranium.
GROUP V.—Lead.
GROUP VI.—Bismuth.
GROUP VII.—Titanium, zirconium, tin.
GROUP VIII.—Palladium, platinum.
GROUP IX.—Rhodium, ruthenium, iridium.

Class IV.

GROUP I.—Lithium, sodium, potassium, rubidium, cæsium, silver.
GROUP II.—Thallium.
GROUP III.—Calcium, strontium, barium.
GROUP IV.—Magnesium, zinc, cadmium.
GROUP V.—Nickel, cobalt.
GROUP VI.—Copper, mercury.
GROUP VII.—Yttrium, cerium, lanthanium, didymium, erbium.
GROUP VIII.—Thorium.

Physical Characters of Chemical Interest.

CRYSTALLIZATION.—Solid substances exist in two forms, *amorphous* and *crystalline*. In the former they assume no definite geometrical shape; they conduct heat equally well in all directions; they break irregularly; and, if transparent, allow light to pass through them equally well in all directions. A solid in the crystalline form has a definite geometrical shape; conducts heat more readily in some directions than in others; when broken, separates in certain directions, called *planes of cleavage*, more readily than in others; and modifies the course of luminous rays passing through it differently when they pass in certain directions than when they pass in others.

Crystals are formed in one of four ways: 1, an amorphous substance, by slow and gradual modification, may assume the crystalline form, as vitreous arsenic trioxide (*q. v.*) passes to the crystalline variety. 2, a fused solid, on cooling, crystallizes, as bismuth. 3, when a solid is sublimed it is usually condensed in the form of crystals. Such is the case with arsenic trioxide. 4, the usual method of obtaining crystals is by the evaporation of a solution of the substance. If the evaporation be slow and the solution at rest, the crystals are large and well-defined. If the crystals separate by the sudden cooling of a hot solution, especially if it be agitated during the cooling, they are small.

Crystallography, treating of the relations of the geometric forms of crystals, has become an extended branch of science, only the fundamental principles and chemical applications of which can be here considered.

Most crystals may be divided by one or more imaginary planes into equal, symmetrical halves; such planes are called *planes of symmetry*. A normal erected upon such a plane and prolonged in both directions until it meets opposite parts of the exterior of the crystal, at equal distances from the plane of symmetry, is called an *axis of symmetry*. When a plane of symmetry contains two or more equivalent linear directions passing through the centre, that plane is the *principal plane of symmetry*, and the axis of symmetry normal to this plane is the *principal axis*.

Upon the relations of these imaginary planes and axes a classification of all crystalline forms into six *systems* has been based. These systems are the following:

First.—The regular or cubic system.—In crystals of this system there are three equal axes crossing each other at right angles. The simple forms are the cube and its derivatives, the octahedron, tetrahedron, and rhombic dodecahedron. The crystals expand equally in all directions when heated, and are not doubly refracting.

Second.—The pyramidal, right square prismatic or tetragonal system

contains those crystals which have three axes placed at right angles to each other—two being equal to each other, and the third either longer or shorter. The simple forms are two prisms, in one of which the equal axes terminate in the angles of the principal plane, and in the other in its sides; and two octahedra, differing from each other in the same way as the prisms. The crystals of this system expand equally only in two directions when heated; they have but one axis of single refraction, and in other directions refract light doubly.

Third.—The hexagonal or rhombohedral system includes crystals having four axes, three of which are of equal length, cross each other at 60°, and in the same plane; to which plane the fourth axis, longer or shorter than the others, is at right angles. The simple forms are the direct dodecahedron, composed of two hexagonal pyramids base to base, in which the equal axes terminate in the angles of the principal plane; the inverse dodecahedron, which differs from the direct in that the axes terminate in the sides of the principal plane; the rhombohedron; and the six-sided prism. The crystals expand equally in two directions when heated; refract light singly through the principal axis, but in other directions refract it doubly.

Fourth.—The rhombic, right rectangular prismatic, or prismatic system.—The axes of crystals of this system are three in number, all at right angles to each other, and differing in length. They, like the two following systems, have no true principal plane or axis. The simple forms are the right rhombic octahedron and the right prism with a rhombic base.

Fifth.—The oblique or monosymmetric system.—The crystals of this system have three axes, two of which cross each other obliquely and at right angles to the third. These axes may be all of unequal length. The simple forms are the oblique octahedron with a rhombic base and the oblique rhombic prism.

Sixth.—The asymmetric, anorthic, or doubly oblique system contains crystals having three axes of unequal length, crossing each other at angles not right angles.

The crystals of the fourth, fifth, and sixth systems, when heated, expand equally in the directions of their three axes; they refract light doubly except in two axes.

It sometimes happens that half the faces of a simple crystal are developed in the formation of a derivative form at the expense of the other half, which are entirely wanting; such a crystal is said to be *hemihedral;* it can be developed only in a system having a principal axis.

Isomorphism.—Although the number of simple forms of crystals is small, the number of their modifications is great; these forms differ from each other in the values of the axes and of the angles of the crystals.

It has been observed that in many instances two or more substances crystallize in forms absolutely identical which each other, and, in most cases, such substances resemble each other in their chemical constitution; they are said to be *isomorphous.* This identity of crystalline form does not depend so much upon the nature of the elements themselves, as upon the structure of the molecule. The protoxide and peroxide of iron do not crystallize in the same form, nor can they be substituted for each other in reactions without radically altering the properties of the resultant compound. On the other hand, all that class of salts known as alums (see p. 383) are isomorphous; not only are their crystals identical in shape, but a crystal of one alum, placed in a saturated solution of another, grows by regular deposition of the second upon its surface. Other alums may

be subsequently added to the crystal, a section of which will then exhibit the various salts, layer upon layer.

DIMORPHISM.—Although most substances crystallize, if at all, in one simple form or in some of its modifications, a few bodies are capable of assuming two crystalline forms belonging to different systems; such are said to be *dimorphous*. Thus, sulphur, as obtained by the evaporation of its solution in carbon disulphide, forms octahedra belonging to the fourth system; when obtained by cooling melted sulphur, the crystals are oblique prisms, belonging to the fifth system. Occasional instances of *trimorphism*, of the formation of crystals belonging to three different systems by the same substance, are also known.

ALLOTROPY.—Dimorphism apart, a few substances are known to exist in more than one solid form. These varieties of the same substance exhibit different physical properties, while their chemical qualities are the same in kind. Such modifications are said to be *allotropic*. One or more allotropic modifications of a substance are *crystalline*, the other or others *amorphous* or *vitreous*. Sulphur, for example, exists not only in two dimorphous varieties of crystals, but also in a third, *allotropic* form, in which it is flexible, amorphous, and transparent. Carbon exists in three allotropic forms: two crystalline, the diamond and graphite; the third amorphous.

In passing from one allotropic modification to another, a substance absorbs or gives out heat.

SPECIFIC HEAT.—Equal volumes of different substances at the same temperature contain different amounts of heat. If two equal volumes of the same liquid of different temperatures be mixed together, the resulting mixture has a temperature which is the mean between the temperatures of the original volumes. If one litre of water at 4° be mixed with a litre at 38°, the resulting two litres will have a temperature of 21°. Mixtures of equal volumes of different substances at different temperatures do not have a temperature which is the mean of the original temperatures of its constituents. A litre of water at 4°, mixed with a litre of mercury at 38°, forms a mixture whose temperature is 27°. Mercury and water, therefor, differ from each other in their capacity for heat. The same difference exists in a more marked degree between equal weights of dissimilar bodies; if a pound of water at 4° be agitated with a pound of mercury at 70°, both liquids will have a temperature of 67°.

The amount of heat required to raise a kilo of water 1° in temperature is a definite quantity. The *specific heat* of any substance is the amount of heat required to raise one kilo of that substance 1° in temperature, expressed in terms having the amount of heat required to raise a kilo of water 1° as unity.

SPECTROSCOPY.—Light in passing through a prism is not only *refracted* into a different course, but is also decomposed or dispersed into different colors, which make up a *spectrum*. A spectrum is one of three kinds: 1st, *continuous*, consisting of a continuous band of colors: red, orange, yellow, green, blue, indigo, and violet. Such spectra are produced by light from white-hot solids and liquids, from gas-light, candle-light, lime-light, and electric light. 2d, *bright-line spectra*, composed of bright lines upon a dark ground, are produced by glowing vapors and gases. 3d, *absorption spectra* consist of continuous spectra crossed by dark lines or bands, and are produced by light which gives a continuous spectrum passing through a solid, liquid, or gas capable of absorbing rays of certain colors.

The solar spectrum belongs to the third class. Fraunhofer was the first to observe that the spectrum of sunlight was not continuous, but interrupted by a great number of black lines, crossing it throughout its length. The more prominent of these lines he designated by the letters A, B, C, D, E, F, G, H, *a*, and *b*. Most of these lines correspond in position with the bright lines produced by the incandescent vapors of various elements.

The spectroscope consists of four essential parts: 1st, the slit, a linear opening between two accurately straight and parallel knife-edges; 2d, the collimating lens, a biconvex lens in whose principal focus the slit is placed, and whose object it is to render the rays from the slit parallel before they enter the prism; 3d, the prism of dense glass, and usually of 60°, so placed that its refracting edge is parallel to the slit; 4th, an observing telescope, so arranged as to receive the rays as they emerge from the prism. In direct vision spectroscopes a compound prism is used, so made up of prisms of different kinds of glass that the emerging ray is in the same straight line as the entering ray.

As the spectra produced by different substances are characterized by the positions of the lines or bands, some means of fixing their location is required. The usual method consists in determining their relation to the principal Fraunhofer lines. As, however, the relative positions of these lines vary with the nature of the substance of which the prism is made, although their position with regard to the color of the spectrum is fixed, no two of the arbitrary scales used will give the same reading.

The most satisfactory method of stating the positions of lines and bands is in wave-lengths. The lengths of the waves of rays of different degrees of refrangibility have been carefully determined, the unit of measurement being the tenth-metre, of which 10^{10} make a metre. The wave-lengths, $=\lambda$, of the principal Fraunhofer lines, are:

A.....	7604.00	D.....	5892.12	G.....	4307.25
B.....	6867.00	E.....	5269.13	H_1.....	3968.01
C.....	6562.01	F.....	4860.72	H_2.....	3933.00
		a.....	7185.0	*b*.....	5172.0

The scale of wave-lengths can easily be used with any spectroscope having an arbitrary scale, with the aid of a curve constructed by interpolation. To construct such a curve paper is used which is ruled into square inches and tenths. The ordinates are marked with a scale of wave-lengths and the abscisses with the arbitrary scale of the instrument. The position of each principal Fraunhofer line is then carefully determined in terms of the arbitrary scale, and marked upon the paper with a × at the point where the line of its wave-length and that of its position in the arbitrary scale cross each other. Through these × a curve is then drawn as regularly as possible. In noting the position of an absorption-band the position of its centre in the arbitrary scale is observed, and its value in wave-lengths obtained from the curve, which, of course, can only be used with the scale and prism for which it has been made.

POLARIMETRY.—A ray of light passing from one medium into another of different density, at an angle other than 90° to the plane of separation of the two media, is deflected from its course, or *refracted*. Certain substances have the power, not only of deflecting a ray falling upon them in certain directions, but also of dividing it into two rays, which are peculiarly modified. The splitting of the ray is termed *double*

refraction, and the altered rays are said to be *polarized*. When a ray of such polarized light meets a mirror held at a certain angle, or a crystal of Iceland spar peculiarly cut (a Nichols' prism), also at a certain angle, it is extinguished. The crystal which produces the polarization is called the *polarizer*, and that which produces the extinction the *analyzer*.

If, when the polarizer and analyzer are so adjusted as to extinguish a ray passing through the former, certain substances are brought between them, light again passes through the analyzer; and in order again to produce extinction, the analyzer must be rotated upon the axis of the ray to the right or to the left. Substances capable of thus influencing polarized light are said to be *optically active*. If, to produce extinction, the analyzer is turned in the direction of the hands of a watch, the substance is said to be *dextrogyrous;* if in the opposite direction, *lævogyrous*.

The distance through which the analyzer must be turned depends upon the peculiar power of the optically active substance, the length of the column interposed, the concentration if in solution, and the wave-length of the original ray of light. The *specific rotary power* of a substance is the rotation produced, in degrees and tenths, by one gram of the substance dissolved in one cubic centimetre of a non-active solvent, and examined in a column one decimetre long. The specific rotary power is determined by dissolving a known weight of the substance in a given volume of solvent, and observing the angle of rotation produced by a column of given length. Then let p=weight in grams of the substance contained in 1 c.c. of solution; l the length of the column in decimetres; a the angle of rotation observed; and $[a]$ the specific rotary power sought, we have

$$[a]=\frac{a}{pl}.$$

In most instruments monochromatic light, corresponding to the D line of the solar spectrum, is used, and the specific rotary power for that ray is expressed by the sign $[a]_D$. The fact that the rotation is right-handed is expressed by the sign +, and that it is left-handed by the sign −.

It will be seen from the above formula that, knowing the value of $[a]_D$ for any given substance, we can determine the weight of that substance in a solution by the formula

$$p=\frac{a}{[a]_D \times l}.$$

Part 2.

SPECIAL CHEMISTRY.

CLASS I.

TYPICAL ELEMENTS.

Hydrogen	H	1
Oxygen	O	16

Although, in a strict sense, hydrogen is regarded by most chemists as the one and only type-element—that whose atom is the unit of atomic and molecular weights—the important part which oxygen plays in the formation of those compounds whose nature forms the basis of our classification, its acid-forming power in organic compounds, and the differences existing between its properties and those of the elements of the sulphur group, with which it is usually classed, warrant us in separating it from the other elements and elevating it to the position it here occupies.

HYDROGEN.

H.....1

Hydrogen exists uncombined in the gases from the fumaroles of Iceland and Tuscany; in combination very abundantly in water, in many organic substances, and in ammoniacal compounds.

Hydrogen is liberated from its compounds:

First.—By the decomposition of acidulated water by the galvanic current, when it is given off from the negative pole. This method is resorted to when chemically pure hydrogen is required.

Second.—By the decomposition of water by the chemical action of certain metals. This takes place either at ordinary temperatures, as in the case of sodium—

$$Na_2+2H_2O=2NaHO+H_2,$$

or at a red heat, as in the case of iron—

$$3Fe_2+8H_2O=2Fe_3O_4+8H_2.$$

Third.—By the decomposing action exerted by certain metals, such as zinc, upon the mineral acids in the presence of water—

$$Zn + SO_4H_2 + xH_2O = SO_4Zn + H_2 + xH_2O.$$

What part the water plays in the reaction is still a subject of discussion; it is probable that its action is rather physical than chemical. Chemically pure zinc, or zinc whose surface has been coated with an alloy of zinc and mercury, does not decompose the acid unless it forms part of a galvanic battery whose circuit is closed. The zincs of galvanic batteries are therefor coated with the alloy mentioned—are amalgamated—to prevent waste of zinc and acid.

This method is the one resorted to for obtaining hydrogen in the laboratory; the gas so obtained is, however, contaminated with small quantities of other gases, hydrogen phosphide, sulphide, and arsenide.

At ordinary temperatures and pressure, and when pure, it is a colorless, odorless, tasteless gas, fourteen and one-half times lighter than air, being the lightest known substance. One litre at 0° and 760 mm. barometric pressure weighs 0.0896 gram, a quantity which forms an important unit of weight, called by Hofmann a *crith* (κριθή = a barley-corn). It is almost insoluble in water and in alcohol. It is a better conductor of heat and electricity than is any other gas. It is the most diffusible of gases, in obedience to the law that the diffusion volume of a gas is in inverse proportion to the square root of its density. The rapidity with which its diffusion takes place renders the use of hydrogen, which has been kept for even a comparatively short time in metallic gasometers, dangerous from the formation of explosive mixtures of air and hydrogen within. India-rubber gas-bags are more dangerous than metallic gasometers.

Hydrogen was formerly supposed to be a *permanent* gas, *i. e.*, not capable of reduction to the liquid or solid state. Recently, however, Cailletet, of Paris, obtained it in the form of a visible cloud; and Pictet, of Geneva, with a pressure of 650 atmospheres and a temperature of −140°, succeeded in reducing it to a steel-blue liquid.

Under ordinary conditions hydrogen exhibits no great tendency to unite with other elements, chlorine being the only one with which it will unite at ordinary temperatures, and that only under the influence of light. At higher temperatures it unites with oxygen.

Mixtures of hydrogen and oxygen remain such indefinitely at ordinary temperatures, but if heated sufficiently even at a single point, as by the passage of an electric spark, a sudden and complete union takes place throughout the mass (if the proportions be H2 to O1), attended by a violent explosion, due to the formation of vapor of water and its sudden expansion under the influence of the intense heat produced by the union. Hydrogen has so marked a tendency to unite with oxygen at high temperatures that many compounds containing oxygen give up that element when heated in an atmosphere of hydrogen:

$$\underset{\text{Cupric oxide.}}{CuO} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Copper.}}{Cu} + \underset{\text{Water.}}{H_2O}.$$

This removal of oxygen from a compound is called a *reduction* or *deoxidation*, and it is by such a process that the reduced iron, or iron by hydrogen of pharmacy, is prepared.

At the instant that hydrogen is liberated from its compounds it has a deoxidizing power similar to that which ordinary hydrogen possesses only

at elevated temperatures. The greater energy of hydrogen, and of other elements as well, in this *nascent state*, may be thus explained: free hydrogen exists in the form of molecules, each one of which is composed of two atoms. At the instant of its liberation from a compound, on the other hand, it is in the form of individual atoms, and that portion of force required to split up the molecule into atoms, necessary when free hydrogen enters into reaction, is not required when the gas is in the nascent state, and consequently a less addition of force in the shape of heat is required to bring about the reaction.

Hydrogen burns in air with a pale but hot flame, the product of the combustion being water. It does not maintain combustion or respiration; a lighted taper is extinguished when immersed in an atmosphere of hydrogen, and under like conditions an animal dies—not from any poisonous action of the gas, but from its inability to maintain the processes of respiration.

In its physical and chemical properties, this element more closely resembles those usually ranked as metals than it does those forming the class of metalloids, among which it is usually placed; its conducting power, its appearance in the liquid form, as well as its relation to the acids, which may be considered as salts of hydrogen, tend to separate it from the metalloids.

Hydrogen is constantly found in small quantity in the gases exhaled from the lungs, as well as in those contained in the stomach and intestines.

OXYGEN.

O.....16

Oxygen is the most abundant of the elements, and exists uncombined in atmospheric air, of which it forms 21 per cent. It also enters into the composition of a vast number of compound substances, mineral, vegetable, and animal.

Although existing in air, and only mixed with nitrogen and small quantities of other gases, no process has yet been devised which can be advantageously used for obtaining oxygen from this source directly. Resource is always had to the decomposition of some substance rich in oxygen.

First.—By heating mercuric oxide (the red oxide) it is decomposed into mercury and oxygen:

$$2HgO=2Hg+O_2.$$

This process is only of historical interest, as being the one by which Priestley first obtained oxygen in 1774.

Second.—By heating manganese dioxide (black oxide of manganese) to redness in an iron or clay retort:

$$3MnO_2=Mn_3O_4+O_2.$$

The yield according to this equation should be 85 litres of oxygen from 1 kilo of the oxide; but, owing to impurities, the amount is much less and the gas is impure.

Third.—By heating manganese dioxide with sulphuric acid in a glass flask:

$$2MnO_2+2SO_4H_2=2SO_4Mn+2H_2O+O_2.$$

The theoretical yield is 128 litres of gas from each kilo of oxide.

Fourth.—The best method, and that generally used, is by the decomposition of potassium chlorate by heat:

$$2ClO_3K = 2KCl + 3O_2.$$

The chlorate yields up all of its oxygen to the amount of 272.6 litres per kilo of chlorate.

The evolution of gas takes place at a lower temperature and much more quietly if the chlorate be mixed with one to two parts by weight of manganese dioxide. At the end of the operation the manganese dioxide remains apparently unaltered, and it is probable that during the action it goes through a series of oscillating oxidations and deoxidations, which take place at a lower temperature than that required for the decomposition of the chlorate alone.

Methods have been suggested by Tessié du Motay, Boussingault, and Mallet, for extracting oxygen from the air, and attempts have been made to utilize these processes in the arts; but the chlorate process is still in general use, on account of its comparative cheapness and the purity of the product.

Oxygen is a colorless, odorless, tasteless gas; liquefies under the combined influence of a pressure of 300 atmospheres and a temperature of —140° (Pictet). The specific gravity of the gas is 1.10563 A,* or 15.95 H,† and that of the liquid 0.9787 (Pictet); 1 litre of the gas at 0° C. and 760 mm. weighs 1.437 gram. It is very sparingly soluble in water, somewhat more soluble in absolute alcohol.

Oxygen is characterized, chemically, by the strong tendency which it exhibits to enter into combination with other elements, only one of which is known, *i. e.*, fluorine, that does not form an oxygenated compound. With most elements it is capable of uniting directly, especially at elevated temperatures. In many instances this union is attended by the appearance of light, and always by the extrication of heat. The luminous union of oxygen with another element constitutes the familiar phenomenon of *combustion*, and is the principal source from which we obtain heat and light. A body is said to be combustible when it is capable of so energetically combining with oxygen as to liberate light as well as heat, Certain gases are said to be supporters of combustion, because combustible substances will unite with them or with some of their constituents, the union being attended with the appearance of heat and light. The distinction between combustible substances and supporters of combustion is, however, one of mere convenience; the action taking place between the two substances, one is as much a party to it as the other.

A jet of air burns in an atmosphere of coal-gas as readily, and with the same luminous flame which is observed when a jet of coal-gas is caused to burn in air.

Oxidations, and indeed, most chemical *unions*, are attended with a liberation of heat; and in some instances, as when powdered antimony is thrown into an atmosphere of chlorine, light is also observed without the occurrence of any oxidation.

The process of respiration is very similar to combustion, and as oxygen gas is the best supporter of combustion, so, in the diluted form in

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* Air unity. † Hydrogen-unity.

which it exists in atmospheric air, it is not only the best, but the only supporter of animal respiration.

Ozone.

Air through which discharges of static electricity have passed assumes a peculiar odor, resembling somewhat that of sulphur; the same odor is perceived in the oxygen obtained by the decomposition of water if the electrodes be of platinum or gold. This odor is due to the conversion of a part of the oxygen into an allotropic modification called *ozone.*

Ozone has not been obtained free from oxygen; indeed, the highest degree of concentration which has been reached does not exceed one per cent. of ozone. Thus diluted, ozone is produced: 1st, by the decomposition of water by the battery; 2d, by the slow oxidation of phosphorus in damp air; 3d, by the action of concentrated sulphuric acid upon barium dioxide; 4th, by the passage of electric discharges through air or oxygen. It is by the last method that ozonized oxygen is usually obtained artificially, and that the traces of ozone existing in the atmosphere are produced.

Ozone is condensed oxygen, as is shown, by the fact that the latter gas contracts when ozonized. When heated to 100° it begins to revert to its primitive form of oxygen, a change which is complete at 237°. It is a powerful oxidizing agent; it converts iodides into iodates; it is destroyed by contact with rubber, cork, and other organic materials, which it oxidizes; it decolorizes organic pigments.

The presence of ozone in air is demonstrated by its action upon a paper impregnated with a mixture of starch and potassium iodide, which turns blue on contact with ozone. To exclude other gases capable of bluing such paper, a faintly red litmus paper, impregnated with potassium iodide to half its extent, is also used; if the bluing of the starch paper be due to ozone, the litmus paper is also blued, and the action upon either paper does not take place after the ozonized air has been heated to 260°.

When inhaled, air containing 0.07 gram of ozone per litre causes intense coryza and hæmoptysis. Its presence in atmospheric air has been considered by some as favoring, and by others as preventive of, contagious diseases; certain it is that, by its oxidizing action, ozone is fatal to the lower forms of animal and vegetable life.

Compounds of Hydrogen and Oxygen.

Two of these are known:
First.—Hydrogen oxide, or water.
Second.—Hydrogen peroxide, or oxygenated water.

Water—H_2O.

Occurrence.—Water exists, widely disseminated and in large quantities, in the three kingdoms of nature, in the three forms of solid, liquid, and gas.

In unorganized nature, water occurs in the gaseous form in atmospheric air (see p. 96), and in the vapors discharged from the earth in volcanic regions. In the liquid form it exists very abundantly, hold-

ing in solution solid and gaseous matter in varying quantities. In the solid form, as ice, at temperatures below 0° C., and also in the form of *water of crystallization*, by which is understood a certain definite quantity of water taken up by many substances when they assume the crystalline form. This water is not in the liquid form at ordinary temperatures, nor yet in the form of ice, but combined with the solid matter of the crystal. Although the chemical nature of the substance is not modified by the presence or absence of water of crystallization, its presence is necessary to the maintenance of the peculiar shape of the crystal. The tenacity with which water of crystallization is held in combination varies in different substances; in some the union is so loose that on exposure to air the crystal loses its water and falls to a shapeless powder; it is then said to *effloresce*. Other crystals, which are said to be permanent in air, only lose their water of crystallization if heated; they then melt, and part or all the water is driven off, leaving a shapeless mass, which is capable of crystallization only when the proper amount of water is again taken up.

In the organized world, water forms a constituent part of every fluid and tissue (see p. 67).

Formation.—Water is produced in a great number of chemical reactions.

First.—Most simply by the direct union of its constituent gases, brought about by elevation of temperature:

$$2H_2+O_2=2H_2O.$$

In obedience to Avogadro's law, the volume of water-gas formed is to the volume of the mixture before union as 2 : 3, provided the mixture originally contained two volumes of hydrogen to one volume of oxygen.

Second.—Whenever hydrogen, or a substance containing hydrogen, is burned in air or oxygen.

Third.—When an organic substance containing hydrogen is heated to redness in the presence of cupric oxide, or of other substances capable of yielding oxygen—

$$\underset{\text{Alcohol.}}{C_2H_6O}+\underset{\text{Cupric oxide.}}{6CuO}=\underset{\text{Copper.}}{6Cu}+\underset{\text{Carbon dioxide.}}{2CO_2}+\underset{\text{Water.}}{3H_2O},$$

a reaction which is utilized for the determination of the amount of hydrogen contained in organic substances.

Fourth.—When an acid and a hydrate react upon each other to form a salt:

$$\underset{\text{Sulphuric acid.}}{SO_4H_2}+\underset{\text{Potassium hydrate.}}{2KHO}=\underset{\text{Potassium sulphate.}}{SO_4K_2}+\underset{\text{Water.}}{2H_2O}.$$

Fifth.—In the reduction of metallic oxides by hydrogen:

$$\underset{\text{Cupric oxide.}}{CuO}+\underset{\text{Hydrogen.}}{H_2}=\underset{\text{Copper.}}{Cu}+\underset{\text{Water.}}{H_2O}.$$

Sixth.—In the reduction and oxidation of a number of organic substances.

Pure water may be obtained either by the union of its elements or by the separation of naturally occurring water from the solid and gaseous substances which it holds in solution and in suspension. The purification of natural water, effected by the processes of filtration and distillation, is the method resorted to in all cases. To obtain water sufficiently pure for chemical purposes, it is boiled in a vessel of tinned copper, called a still, and the vapor is directed through a tube, around which cold water is made to circulate, and in which the vapor is condensed to the liquid form. The condensing tube is usually of block-tin, or, preferably, of glass. The first 10 per cent. of condensed water is rejected, as it contains air, carbon dioxide, ammonia, and many volatile substances which the water may have held in solution. The following 70 per cent. of the original volume is collected for use, the distillation being stopped while 20 per cent. of the original water remains in the still.

Distilled water so obtained should be perfectly clear, colorless, odorless, and tasteless, and should leave no residue when a small quantity is evaporated upon platinum foil. Although ordinary distilled water is sufficiently pure for most chemical purposes, it is not absolutely free from impurity, and when evaporated in a platinum basin it leaves more or less residue. To obtain a chemically pure water is a matter of some difficulty. Distilled water should be used in the preparation of all aqueous solutions intended for use in chemical manipulations.

Physical properties.—At temperatures below 0° C., with a barometric pressure of 760 mm., water assumes the solid form; between 0° and 100° it is liquid; and at temperatures above 100°, the pressure remaining the same, it is gaseous. The freezing and boiling points are modified by the barometric pressure, and by the presence of solid matter in solution in water. The freezing-point is, under ordinary conditions, at 0° of the Centigrade scale, and at 32° of the Fahrenheit. Under certain conditions, as when enclosed in capillary tubes and at complete rest, it may be cooled as far as −15° C. without solidifying. If water so cooled be agitated, it solidifies instantly, and the temperature suddenly rises to 0°.

In solidifying, water is rather suddenly expanded, and this expansion takes place with great force; for this reason ice is lighter than water at any temperature below 8.5°, and consequently floats. Water is at its densest at 4° C. The solidification of water is a crystallization; the form of the crystals, which belong to the hexagonal system, may be readily observed in snow, or even, under suitable conditions, in ice, which is composed of closely applied crystals.

The boiling-point is subject to much greater variations than the freezing-point; it falls, with diminutions of pressure, to the extent of about 1° C. for each fall of 25 mm. of pressure. Conversely, as the pressure is increased the boiling-point rises, attaining 200° with a pressure of between fifteen and sixteen atmospheres. Advantage is taken of the fall of the boiling-point with diminished pressure to measure the altitude of mountains, upon the tops of some of the higher of which boiling water is not hot enough to be of service in culinary operations. The increased temperature which may be imparted to liquid water under pressure is utilized in many processes in the laboratory and in the arts, for effecting solutions and chemical actions which do not take place at lower temperatures. The boiling-point of water holding solid matter in solution is higher than that of pure water, the degree of increase depending upon the amount and nature of the substance dissolved. On the other hand, mixtures of water with liquids of lower boiling-point boil at tempera-

tures less than 100°. Although the conversion of water into water-gas takes place most actively at 100°, water and ice evaporate at all temperatures.

One of the most important physical properties of water is its high rank as a solvent, there being comparatively few substances, solid, liquid, or gaseous, which are absolutely insoluble in it. The solution of a substance in water may take place in two very different ways. The action may be partly chemical, as when barium oxide is dissolved in water, combination of the two substances taking place with formation of barium hydrate—

$$BaO+H_2O=BaH_2O_2,$$

which is subsequently dissolved. In solutions of this kind, as in other instances where chemical union takes place, the action is accompanied by an *increase* of temperature. In true simple solutions, on the other hand, as when common salt is dissolved in water, there is no chemical action; no increase, but, on the contrary, a diminution of temperature.

The quantity of a substance which a given volume of water is capable of dissolving depends upon the nature of the substance, the temperature, the presence or absence of other substances already in solution, and the presence or absence of another solvent. Some substances are much more soluble in water than others; barium sulphate is insoluble in water, while calcium chloride has such an avidity for the solvent that, when exposed to the air, it quickly absorbs sufficient water therefrom to form a solution. That passage of a solid into solution in absorbed water is known as *deliquescence.* As a rule, the power of water to dissolve solids increases with the temperature, while the solubility of gases in water is greater at low than at high temperatures. The quantity of any substance which a given volume of water will dissolve at a given temperature is definite; and when this quantity has been dissolved, the solution is said to be *saturated;* it is only so for that degree of temperature at which it has been made. Saturated solutions of solids, as a rule, can be made to dissolve further quantities by elevation of temperature, or to deposit that which they already hold by cooling. Saturated solutions of gases are modified by variations of temperature in the opposite way. In the cases of certain salts, solutions saturated at high temperatures may be cooled without depositing any of the salt; they thus become at lower temperatures *supersaturated* solutions; containing more of the salt than they could be made to dissolve at the temperature to which they have been cooled. A saturated solution of one substance in water is often capable of dissolving considerable quantities of another substance, and of then becoming capable of taking up a further quantity of the first substance. The power of water to dissolve gases increases with increased pressure. Fats, resins, and, in general, organic substances containing a large number of carbon atoms, are insoluble in water.

Vapor of water is colorless, transparent, invisible (the white cloud, usually called steam, is produced by the condensation of vapor of water into minute liquid drops); its specific gravity is 0.6234A=1 or 18—H=2. A litre of vapor of water weighs (reduced to 0° and 760 mm.) 0.8064, or nine times as much as an equal volume of hydrogen.

The latent heat of vaporization of water is 536.5; that is, as much heat is required to vaporize 1 kilo of water at 100° as would raise 536.5 kilos 1° C. in temperature. In passing from the liquid to the gaseous form, water expands 1,696 times in volume.

Chemical properties—Decompositions.—First.—By passing the current of a galvanic battery through acidulated water, two volumes of hydrogen are given off at the zinc or negative pole, and one volume of oxygen at the platinum or positive pole.

Second.—By passing vapor of water through a platinum tube heated to whiteness, or through a porous porcelain tube heated to about 1,100° (Deville).

Third.—By acting upon water at low temperatures with the alkaline metals, hydrogen is given off, and a hydrate of the metal remains in solution in the excess of water:

$$\underset{\text{Water.}}{2H_2O} + \underset{\text{Potassium.}}{2K} = \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{2KHO} + \underset{\text{Hydrogen.}}{H_2}.$$

Fourth.—By passing vapor of water over iron heated to redness, an oxide of the metal is formed and hydrogen liberated (see p. 33).

Other reactions.—First.—Water combines with many metallic oxides to form compounds known as hydrates, which may be considered as molecules of water in which one-half the hydrogen has been replaced by an equivalent quantity of the metal. When the metal is univalent, the action takes place between single molecules of oxide and water, with the formation of two molecules of hydrate; or, in other words, the hydrate is formed by the substitution of an atom of metal for one atom of hydrogen in a single molecule of water:

$$K_2O + H_2O = 2KHO;$$

or,

$$\underset{\text{Potassium oxide.}}{\left.\begin{matrix}K\\K\end{matrix}\right\}O} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} = 2\underset{\substack{\text{Potassium}\\\text{hydrate.}}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)}$$

When the metal is divalent, the action still takes place between single molecules of water and oxide, but with the formation of a single molecule of hydrate; or, in other words, the hydrate is formed by the substitution of an atom of the divalent metal for a double atom of hydrogen in a double molecule of water:

$$CaO + H_2O = CaH_2O_2;$$

or,

$$\underset{\substack{\text{Calcium}\\\text{oxide.}}}{\left.\begin{matrix}Ca\\O\end{matrix}\right\}} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} = \underset{\substack{\text{Calcium}\\\text{hydrate.}}}{\left.\begin{matrix}Ca\\H_2\end{matrix}\right\}O_2}.$$

Second.—Water combines also with the oxides of those elements usually classed as metalloids, with the formation of hydrates which differ very materially in their chemical properties from the hydrates of the metals. It combines with the oxides of sulphur and phosphorus to form the acids of those elements:

$$\underset{\substack{\text{Sulphur}\\\text{trioxide.}}}{SO_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{SO_4H_2} \qquad P_2O_5 + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{2PO_4H_3}.$$

$$\underset{\substack{\text{Phosphorus}\\\text{pentoxide.}}}{}$$

Certain of these acids are capable of combining chemically with a greater number of molecules of water to form what are known as hydrates of the acids. Thus, there are definite hydrates of sulphuric acid having the formulæ—

$$SO_4H_2,\ H_2O \text{ and } SO_4H_2,\ 2H_2O,$$

which differ materially in their physical properties from the acid SO_4H_2. That these hydrates are not mere mechanical mixtures is shown by the fact that their formation is attended by the liberation of heat.

Third.—Certain substances exhibit a great tendency to absorb water from surrounding bodies, and are therefor used as drying agents; calcium chloride, sulphuric acid and phosphorus pentoxide are used for drying gases in the laboratory. The preservative action of alcohol upon animal substances is largely, if not entirely, due to its power of absorbing water, and thus, in a manner, drying the putrescible substances.

Fourth.—The chlorides of the elements of the third and fourth classes are either insoluble in water, or soluble without decomposition; the corresponding compounds of the second class are decomposed when brought into contact with water:

$$\underset{\text{Phosphorus trichloride.}}{PCl_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphorous acid.}}{PO_3H_3} + \underset{\text{Hydrochloric acid.}}{3HCl}.$$

Natural Waters.

From whatever source natural water is obtained, it always holds solid and gaseous matter in solution, and very frequently solid matter in suspension as well. The amount and nature of the substances held in solution vary greatly with the purity and temperature of the atmosphere through which the water has fallen as rain, with the nature of the geological strata through or over which it has passed, and with the geographical position of the source from which it is obtained.

Natural waters may be divided into *potable* and *unpotable* waters. To the first class belong: 1st, rain-water; 2d, snow- and ice-water; 3d, spring-water (fresh); 4th, river-water; 5th, lake-water; 6th, well-water. To the second belong: 1st, stagnant waters; 2d, sea-water; 3d, mineral-spring waters.

First.—Rain-water varies much in purity according to the localities in which it is collected and the condition of the atmosphere at the time. It holds in solution comparatively small quantities of solid matter, consisting of chlorides, sulphates, and nitrates of sodium and ammonium. The amount of hydrochloric acid is greatest in the neighborhood of salt water, while the sulphate and nitrate of ammonium are most abundant in the rain-water collected in cities.

The following table of analyses, by Dr. R. Angus Smith, indicates variations in the quantity of solid matter in rain-water from different localities:

RAIN-WATER.—AVERAGE IMPURITIES PER MILLION PARTS.

Where collected.	Hydrochloric acid.	Sulphuric acid.	Sulphuric acid for 100 hydrochloric.	Free acids calculated as sulphuric acid.	Ammonia.	Albuminoid ammonia.	Nitric and nitrous acids.
Ireland, Valencia	48.67	2.73	6	none.	.18	.03	.37
Scotland, five sea-coast country places west	12.28	3.61	29	.14	.48	.11	.37
Scotland, eight sea-coast country places east	12.91	7.66	59	2.44	.99	.11	.47
Scotland, twelve inland country places	3.38	2.06	61	.31	.53	.04	.31
England, twelve inland country places	3.99	5.52	138	none.	1.07	.11	.75
Scotland, six towns (Glasgow excluded)	5.86	16.50	282	3.16	3.82	.21	1.16
Darmstadt	.97	29.17	2998	1.74	....	...	....
London	1.25	20.49	1645	3.10	3.45	.21	.84
England, six manufacturing towns	8.70	34.27	394	8.40	4.99	.21	.85
Manchester	5.83	44.82	768	10.17	5.96	.25	1.01
Glasgow	8.97	70.19	782	15.13	9.10	.30	2.44

In commenting upon these results, Dr. Smith observes that the amount of chlorides is dependent upon the distance from the sea and the direction of the prevailing winds; that the sulphuric acid increases as we go inland, and is derived partially from the combustion of coal, and partially from the decomposition of organic matter; and that when the proportion of sulphuric acid to hydrochloric acid is greater than 11.6 to 100. the presence of the excess of the former is due to terrestrial contamination,

The presence of nitrate and nitrite of ammonium is due, to a certain extent, to the decomposition of organic matter, but principally to the combustion of coal, as is shown by the large quantity existing in the rain-water collected in manufacturing towns, and by the greater proportion of ammonia found in rain-water in Lyons, by Bineau, in winter than in summer:

Winter.	Spring.	Summer.	Autumn.	Average.
16.3	12.1	3.1.	4.0	6.8

As, during its formation in and passage through the atmosphere, rain-water exposes a large surface, it dissolves, besides solids and vapors, comparatively large quantities of gases—oxygen, nitrogen, carbon dioxide, and, over cities, sometimes hydrogen sulphide and sulphur dioxide —the last-named gases being produced by the combustion of coal containing sulphides. According to Péligot, a litre of rain-water at Paris contains 2.4 c.c. carbon dioxide, 6.59 c.c. oxygen, and 14.0 nitrogen. According to Gérardin, rain-water at the same place contains from 5.18 c.c. to 8. c.c. of oxygen per litre. Great care should be taken, in the collection of rain-water, that it should not be allowed to come into contact with lead surfaces, as the comparatively small quantities of carbon dioxide and carbonates, and the comparatively large quantities of oxygen and nitrates which it contains, render it peculiarly prone to contamination with that metal (see p. 56).

Rain-water is liable to contain notable quantities of organic matter, especially in summer, in the shape of vegetable spores, which it holds in suspension; the presence of these bodies renders the water liable to become stale when kept.

Second—Melted snow and ice.—The waters obtained from these two sources differ much from each other as to their purity. That obtained from ice is of great purity, so far as dissolved matters go; for these, during crystallization, are to a great extent, although not completely, separated from the ice and retained in the unfrozen water. Hassall states that in freezing a small portion of water the following separation took place:

	Original water.	Ice.	Remaining water.
Total solids.....	27.0	3.0	14.2
Chlorine	1.94	0.9	....
Lime	10.53	trace	14.11

Water obtained by melting the ice of sea-water is used for drinking-water in the Arctic regions. Owing, however, to the separation of the dissolved gases together with the solids, ice-water has a flat taste.

The water obtained from melted snow contains about the same proportion of fixed solid matter as rain-water, but a less proportion of ammoniacal salts and of gases:

	Sodium chloride.	Ammonium bicarbonate.	Ammonium nitrate.
Snow-water.....	0.01704	0.00129	0.00145
Rain-water.....	.....	0.00087	0.00189

	Sodium sulphate.	Calcium sulphate.	Organic matter.
Snow-water.....	0.01563	0.00088	0.02385
Rain-water.....	0.01007	0.00087	0.02486

In high, mountainous regions, the drinking-waters used are largely mixtures of melted ice and snow, and many observers have attributed the goitre and cretinism prevailing in these locations to the use of such water (see p. 50).

Third.—Spring-water is simply rain-water which has percolated through the subjacent strata, and, owing to the conformation of the ground and the arrangement of the strata, has made its appearance upon the surface at some level below that upon which it originally fell. During its passage through the earth, in which it is frequently subjected to pressure, it dissolves solid and gaseous matter, varying in kind and in quantity with the nature of the strata with which the water has been in contact, the duration of such contact, and the pressure to which it is subjected.

The amount of extraneous matter dissolved in spring-water, therefor, varies greatly—from the water of some saline springs, which are almost saturated solutions of sodium chloride, to the pure spring-water which flows from the side of a porphyritic or quartz mountain. Between these extremes are waters of all degrees of purity.

Spring-waters from igneous rocks and from the older sedimentary formations are sweet, and any spring-water may be so considered whose temperature is below 20° and which does not contain more than 0.4

gram of solid matter in the litre; provided, however, that a large proportion of this solid residue is not composed of salts having a medicinal action, and provided also that it does not hold sulphurous gases or sulphides in solution. The mineral water of Plombières contains only 0.24 gram of solid matter to the litre; but of this, 0.0927 gram is sodium sulphate; the waters of Bagnères contain only 0.227 gram solid matters, of which 0.064 gram is composed of sulphides; it also has hydrogen sulphide in solution.

As a rule, the water of "fresh" springs is cool even in summer, contains a much less proportion of solid matter than that mentioned above, and has a crisp and agreeable flavor, owing to the almost entire absence of organic matter and the presence of a comparatively large amount of dissolved oxygen. Spring-waters from limestone and dolomite formations contain excessive quantities of the salts of magnesium and calcium, in consequence of which, without being valuable as "mineral waters," their usefulness as drinking-water is greatly diminished or destroyed (see p. 49).

Artesian wells may be regarded as artificial springs, formed by boring perpendicularly into the earth, in a low-lying district surrounded by more elevated ground, until a permeable layer included between two strata of impermeable rock is reached, the strata being so curved that their outcrop is in the surrounding elevated district. When such a well has been successfully bored, usually at great cost, it furnishes, without pumping, an abundant supply of water, more or less pure, according to the nature of the strata through which the water has percolated. The following table indicates the nature of the impurities present in the waters from springs and artesian wells:

Origin.	Fixed residue.	Ca.	Mg.	Cl.	Organic matter.	Authority.
Spring near Besançon, France	0.3085	0.1046	0.0008	0.0016	.....	H. Deville.
Spring in Surrey, England.	0.225	0.0626	0.0025	0.0121	0.0136	Graham, Miller & Hofmann.
Spring near Auburn, Me...	0.0349	.....	.....	.....	0.0022	S. D. Hayes.
Artesian well at Grenelle, France	0.143	0.0272	0.004	0.0052	0.002	Payen.
Artesian well at Trafalgar Square, London.....	0.9915	0.0188	0.0091	0.1742	0.013	Abel & Rowney.
Artesian well at Dedham, Mass.....	0.0888	.....	.....	.....	0.019	S. D. Hayes.
Artesian well at Boston....	0.945	.....	.....	.....	0.0317	"
Brewery Spring, Boston....	0.2629	.....	.....	.....	0.0288	"

Some of these artesian wells are of great celebrity: that at Grenelle, in the outskirts of Paris, has a depth of 1,748 feet, and furnishes 516 gallons per minute, the water rising to a height of 32 feet from the level of the ground.

Fourth.—River-water is composed of spring-water, rain-water, and the drainage-water from the country through which the river flows; it contains also ice- and snow-water at all seasons, if the origin of the river be from a glacier or from above the snow-line; and in the lowlands in winter and early spring; or sea-water, if it be sufficiently near the ocean to be under tidal influence. River-water may, therefor, be excellent or entirely unfit for drinking. A river flowing rapidly through a granitic region

distant from the sea, furnishes, unless polluted by man, a pure, bright, and highly aërated water; while another, flowing sluggishly through rich, alluvial lands, yields a muddy, unaërated water, holding large quantities of mineral and organic matter in solution and in suspension.

The amount of mineral matter held in solution in river-water increases with the distance it has travelled. The water of a mountain torrent in the valley of the Isère, near its origin in a glacier, was found by Grange to contain 0.0201 gram of mineral matter per litre; the water from the same stream, 2,000 metres (1¼ mile) below, contained 0.0753 gram per litre. The waters of the Rhine at Bâle contain 0.1694 gram of fixed residue per litre (Pagenstecher); at Strasbourg, about 80 miles below, 0.2317 gram (H. Deville); and at Emmerich, about 400 miles below, 0.289 gram (Müller). The purity of river-water depends largely upon the density of the population, and upon the nature of the industries followed upon its banks; indeed, the two principal sources of the pollution of river-waters are the discharge into them of the sewage of cities and the waste products of factories. In its passage through a large city, river-water receives organic matter, ammonia, chlorides, sulphates, phosphates, and carbon dioxide, while it loses oxygen. The amount of free nitrogen remains nearly the same. In the following table, compiled from the analyses of R. A. Smith, Graham, Miller and Hofmann, and Ashley, are indicated the changes which take place in the amounts of extraneous substances dissolved in the water of the Thames, produced during its passage through London—these changes occurring notwithstanding the fact that the sewage is discharged outside of the city, at a point below Woolwich, distant about twelve miles from London Bridge, and that the contamination is caused by the addition of a quantity of filth exceedingly small as compared with the total sewage of the city.

Water taken at	O.	N.	CO_2	Solids.	Cl.	Organic matter.
Hammersmith....	4.1	15.1	....	....	....	....
Chelsea.....	...	....	0.46	0.304	0.0175	0.034
Waterloo Bridge..	1.5	16.2	....	....	....	....
London Bridge...	...	....	27.2	0.4084	0.0636	0.100
Woolwich.....	0.25	14.5	....	....	....	....

The amounts of dissolved gases are given in c.c., and those of the solids and chlorine in grams per litre.

The question of the most advantageous disposal of the sewage of towns and cities is one which, although it has been the subject of a vast amount of discussion and investigation, is still *sub judice*. If, as is unfortunately often the case, the sewage is discharged into the nearest stream, the water is contaminated to such an extent that it is not only useless for drinking, but also a stench in the nostrils of the inhabitants below. There is also an economic objection to this plan, in that a large quantity of valuable fertilizer is thus wasted. Methods have repeatedly been suggested and subjected to the test of experiment, for utilizing human excreta as fertilizers. These are of four kinds, and, unfortunately, are all open to objections more or less serious.

In Holland and Belgium a very primitive method is followed: the de-

jections are collected in cisterns or barrels, whence they are removed to larger depots, at which the farmers purchase their supplies as needed—using the material without any preparation beyond fermentation and dilution with water. In Paris the excreta are not allowed to enter the sewers, but are collected in cisterns, whence they are pumped at night and carried to a suburb, which will be easily recognized by the traveller, be he never so severely afflicted with catarrh. Here the liquid portions are separated and sold for manure under the name of "eaux vannes," and the solid portions are subjected to a slow drying process, to yield a brown, odorless fertilizer called "poudrette." These two methods of dealing with human excreta from cities are open to the serious objection that the material is allowed to collect and exhale its noxious and disgusting effluvia in the midst of the population, an objection most serious among the poorer householders, who, to avoid the expense of frequent cleansing of the cisterns, fail to use the necessary quantity of water for flushing the closets.

Of late years frequent attempts have been made to use the mixture of surface-water and excreta collected from the sewers by discharging it directly upon the land. Experiments upon a large scale have been made in the neighborhood of Milan, of Edinburgh, of Banbury, at Norwood, and at the Lodge Farm, near London. This plan, which was not attended with the financial success expected by its promoters, is also open to serious objections from a sanitary point of view. It is certainly as favorable to the propagation of disease, especially cholera, typhoid, and entozoic diseases, as is the method of discharging the sewage into the rivers.

A plan which is destined to yield the best results, when all idea of attempting to follow it with pecuniary profit as the principal object shall have been abandoned, is that of collecting the sewage at some point in the neighborhood of the city, and there subjecting it to disinfection with a view to rendering its subsequent use as a fertilizer safe and inoffensive.

It is an undeniable fact that organic matter in solution or in suspension in rapidly moving water is decomposed and oxidized more or less quickly; urea is soon decomposed into carbonic anhydride and ammonia; albuminoid substances are much more slowly oxidized, their nitrogen being converted into nitrates, nitrites, and ammoniacal compounds. Although this decomposition takes place in the course of a few miles in a stream whose current is rapid, provided the admixture of sewage-matter be not in too great proportion, it is impossible to state at what a distance from the source of contamination the water of a river receiving sewage during an epidemic of typhoid or of cholera, would become incapable of communicating the disease, if, indeed, there be any limit.

Quite as serious a source of contamination of river-water exists in the discharge into it of the waste products from factories, etc. These contaminations are as various in their nature as the processes which give rise to them; the question of their disposal is, although much more simple than that in which sewage is concerned, not likely to be quickly solved, owing to the magnitude of the financial interests involved. Manufacturers should be obliged to discharge their waste products, when these are of such a nature as neither to contaminate the air, nor yet to impede navigation, only into rivers whose waters are naturally unfit for drinking. When from any cause this course cannot be followed, they should adopt some process (which will certainly be devised *pro re nata*) of disposing of their refuse in such a way as to avoid pollution of the water.

The nature and amount of the substances held in solution in river-

water varies materially with the season. The warmer the water the more solid and the less gaseous matter it contains. In warm weather the tendency of organic matter to putrefaction is greater, as is also the rapidity of its destruction by oxidation. During those periods when water-courses are swollen by rains and by the melting of snow, the amount of *dissolved* solid matter is relatively diminished, while the amount of *suspended* solids is increased. River-water, at the first part of the flood period, contains an amount of chlorine much greater in proportion to total solids and to hardness than at other periods. The water which comes down during the first part of the flood has not penetrated deeply into the earth, and has therefor had but little opportunity of becoming charged with earthy salts; it has, however, dissolved the more soluble chlorides from the surface. At later periods the water, penetrating more deeply below the surface, becomes more highly charged with calcareous salts.

Fifth—Lake-water.—Fresh lakes, being, as a rule, simply expansions of rivers, or points where many of their tributaries unite, their water is very similar to that of the rivers flowing into or out of them, with the exception that, as the lakes expose a large surface to the air, and as the water is kept in motion both by the current and by the action of the winds, the removal of organic matter by oxidation is more active than in rivers not having a very rapid current. Lakes form natural reservoirs from which the water-supply of many cities is obtained. Those cities situated upon the borders of large lakes are assured of an abundant supply of pure water, it being only required to raise it to a sufficient height for distribution. Municipalities less fortunately situated resort to the construction of more or less elaborate works, for the collection and storage of water from a system of lakes and rivers.

Sixth—Well-water may be very good or very bad. In some instances the well is simply a collecting reservoir dug over a natural spring. When this is the case, if it be in such a situation as to be free from contamination, the water is essentially spring-water (*q. v.*). In most cases, however, a well is simply a hole, deep or shallow, with walls well or badly constructed, into which the surface-water percolates from the thin stratum through which the well is dug. Such water is almost always highly charged with organic matter, insipid or sweetish in taste, and should be carefully avoided.

But the character of well-water, whatever its source, depends largely upon its position. As a rule, wells are constructed near to human habitations, and are thus very liable to contamination with organic matter, either from the surface, or, more frequently, by the breaking of a house-drain and the filtration of its contents, through a few feet of intervening soil, into the water of the well (see p. 52).

Of late years "driven wells" have been largely resorted to in this country. They are formed by driving a pointed iron tube into the earth, increasing the length of tube by sections and removing any earth which may have found its way within the tube, until a supply of water is obtained, either by its spontaneous rise in the tube, or, more commonly, by pumping. The water so obtained is similar in character to that from surface-wells, and, while it may be good where the location is in an open and unmanured location, it is to be looked upon with grave suspicion if the well be driven in any situation where the surface-water is liable to become contaminated with the excreta of men or animals.

Impurities in Potable Water.

Characters of a good water.—It should be cool, limpid, and odorless. It should have an agreeable taste, neither flat, salty, nor sweetish, and it should dissolve soap readily, without the formation of insoluble, flocculent material. Any water which does not possess these qualities is not fit for drinking; but it is by no means true that any water which *does* possess them is not to be looked upon with suspicion. To determine whether or no any given water is potable, a more careful examination into the nature and quantity of foreign substances present is necessary. These substances may be either in solution or in suspension.

First—Total solids.—We have seen that all natural waters are more or less charged with solid mineral matter, a certain proportion of which seems to be necessary to health. On the other hand, if the amount of solid matter dissolved be excessive, the water is both unpalatable and unhealthy. In the following table is given the number of grams per litre of total solids in various waters:

Distilled water	0.0017	Croton	0.0918
London—Thames Co.	0.2646	Boston—Cochituate	0.0548
London—New River Co	0.2509	Charlestown—Mystic	0.0972
London—Kent Co	0.3780	Copenhagen	1.700
Rhine, at Basle	0.1694	Atlantic—surface	34.700
Seine, at Bercy	0.2544	Dead Sea—surface	27.078
Spree, at Berlin	0.114	Dead Sea—300 metres	278.135
Glasgow—Loch Katrine	0.0328		

The amount of total solids in potable waters varies from 0.05 to 0.4 gram per litre, the amount being, as a rule, less in the waters supplied to American cities than in those consumed by the urban populations of Europe. The solids dissolved in water, their nature not being taken into consideration, do not impair its usefulness as a drink, unless they be present in a quantity greater than 0.4 to 0.5 gram per litre.

The determination of the amount of total solids is easily conducted: 25 c.c. of the filtered * water are evaporated to dryness in a previously weighed platinum dish over a water-bath. After cooling in a drying-box, the dish, with the contained residue, is weighed; the increase in weight, multiplied by 40, gives the amount of total solids per litre.

Second—Hardness.—Of the solid matters dissolved in potable waters, the greater part is usually made up of salts of calcium, accompanied, as a rule, by small quantities of salts of magnesium. The calcium salt present is usually the carbonate or the sulphate; sometimes the chloride, phosphate, or nitrate. Calcium carbonate is almost insoluble in pure water; but in water charged with carbon dioxide a more soluble bicarbonate is formed, which remains in solution until the carbon dioxide is expelled by heat, whenever the carbonate is present in quantity greater than 0.5 gram per litre. The sulphate is present, being sparingly soluble, in many excellent waters. In quantity it should not exceed 0.02 gram per litre. The presence of the phosphate is probably more general than published analyses would lead one to suppose, as it is widely disseminated

* Suspended solids must be determined by the method given on p. 57.

in the mineral world, and the processes used for determining phosphoric acid lack accuracy when applied to such small quantities as we have here to deal with. The chloride is rarely present, and only in small quantity. The nitrate is only found in waters contaminated with organic matter, at the expense of whose nitrogen the nitric acid is formed by oxidation.

A water which contains an excess of calcium salts is said to be *hard*, while one not so charged is said to be *soft*. If the hardness be due to the presence of the carbonate, it is *temporary*, as, upon the application of heat, carbon dioxide is driven off, and the excess of carbonate, being no longer soluble, is precipitated. A permanently hard water owes its hardness to the presence of the sulphate, which remains in solution after heating, being dissolved simply by virtue of its own solubility.

It is a matter of common experience that a hard water is not as serviceable for domestic purposes as soft water. If we attempt to dissolve soap in a water charged with calcic and magnesic salts, the first portions are decomposed with the formation of the insoluble calcium and magnesium palmitate and oleate, which separate as flocculent precipitates, and not until the earthy salts have thus been removed will the water be capable of dissolving or forming a lather with soap. Vegetables, when boiled in hard water, do not soften as readily as when the water is soft; moreover, a hard water is difficult of digestion, and is liable to produce disorders of digestion, especially in those unaccustomed to its use.

Magnesium salts, sulphate and carbonate, frequently accompany the corresponding calcium compounds, although in much smaller quantity. Their influence upon the quality of the water is the same as that of the calcium salts, with the difference that if the quantity of magnesic salt exceeds 0.02 gram per litre, the water is to some extent purgative. The opinion advanced by Grange and sustained by others, that the occurrence of goitre and cretinism is due to an excess of magnesium salts in the water, is not well founded. Analysis has shown the presence of greater quantities of magnesium salts in the water of districts where these diseases are unknown than exists in the waters used in localities where they are very prevalent.

Although an excess of calcareous salts in water renders it unfit for domestic use, within proper limits, 0.3 gram per litre, the carbonate and phosphate of calcium are not only not deleterious, but beneficial constituents, as they supply a proportion of those salts required by the economy, especially in the first years of life.

It is rarely necessary to determine the amount of calcium and magnesium salts present in water with accuracy. It is, however, frequently of importance to determine the degree of hardness, which may be measured with tolerable exactness by means of a process suggested by Dr. Clark in 1847, and based upon the soap-destroying power of the earthy salts. The method, as given by Wanklyn and as usually applied, is very simple. Seventy cubic centimetres of the water to be tested are placed in a glass-stoppered bottle having a capacity of 250 c.c. From a burette an alcoholic solution of soap is added, and after each addition the bottle is shaken and laid upon its side for five minutes. If at the end of that time the lather remains, enough soap-solution has been added; if not, the addition must be continued until the lather persists for five minutes. If more than 16 c.c. of soap-solution are used, 70 c.c. of distilled water must be added, as a lather is not readily formed if the proportion of alcohol become too great. Having added sufficient soap-solution, the degree of hardness is indicated by the number of cubic centimetres of soap-solution used minus 1. Thus, if 15 c.c. soap-solution have been used, the degree of hardness is 14.

If from the degree of hardness we subtract 1, we have approximately the number of grains of calcium carbonate, or of salts having an equal soap-destroying power, in a gallon of the water.

To prepare the soap-solution, air-dried white castile soap is reduced to thin shavings, of which 10 grams are dissolved in a litre of weak alcohol, having a specific gravity of about 0.949. The solution must not be filtered; usually it is clear, but, if turbid, it should be shaken before using.

Having made the soap-solution, it is necessary to determine its actual strength, as soap is a substance which cannot be accurately weighed. To this end a solution of calcium chloride of known strength is made by dissolving 1.11 gram of pure, recently fused calcic chloride in a litre of water; 10 c.c. of this solution, mixed with 60 c.c. of distilled water, should require, for the formation of a persistent lather, 11 c.c. of soap-solution. If more or less of the soap-solution be required, it must be concentrated or diluted in the proportion of the deficiency or excess to bring it to the proper strength.

By this method the total hardness is determined. If it be desirable to know what portion of this is temporary or permanent, the total hardness is first determined. Another sample of the water is then boiled, and from this 70 c.c. are taken after filtration, in which the permanent hardness is determined as above; the difference is temporary hardness.

It sometimes occurs that a water, comparatively pure as to organic matters, exhibits a tendency to produce diarrhœa; in this case it is well to determine the amount of magnesian salts present. A litre of water is evaporated to dryness in a platinum dish; the residue is moistened with hydrochloric acid, a small quantity of water is added, and the solution filtered. To the united filtrate and washings ammonium hydrate and solution of ammonium oxalate are added in excess; the liquid is then heated and filtered. To the filtrate more ammonia is added, and the mixture allowed to stand. If after twelve hours a precipitate have formed, the fluid is again filtered. To the clear liquid, which should not be more than 40 c.c. in bulk, solution of phosphate of sodium and ammonium hydrate are added in excess, and the mixture set aside for twenty-four hours. The precipitate is now collected on a filter, washed with ammoniacal water, dried, ignited, and weighed. The weight of the residue, multiplied by 0.36036, equals the weight of magnesia in a litre of the water.

A good drinking-water should not have a hardness of more than 15, and should not contain more than 0.015 gram per litre of magnesium.

Third— Chlorides.—The chlorides of the alkaline and earthy metals occur in varying quantity in all natural water. The occurrence of these salts in quantities not sufficient to render their presence readily detectable by the taste is of no importance *per se;* but, in connection with the presence of organic matter, a determination of the amount of chlorine affords a valuable index to the probable source of the organic matter. The most dangerous of organic contaminations is that by admixture of animal excreta; the presence of vegetable organic matter is, comparatively speaking, innocuous. Vegetable contamination brings with it a very small amount of chlorine, while urine, which, when the water is polluted with sewage, forms the bulk of the contaminating admixture, contains large quantities of chlorides. If, therefor, a well-water be found to contain an excess of chlorides, it is to be looked upon with suspicion; and if at the same time there be an excess of nitrogenized material, there remains but small doubt that the well contains diluted urine. So true is this that at times, when results must be obtained rapidly, as during an epidemic, the

urse for the analyst to pursue is to determine *the amount of* in each source of supply, and to condemn those *containing more* 5 gram per litre (one grain per gallon) of chlorine. *Whenever* ssible, however, a determination of organic matter *should be made,* result considered in connection with the quantity of *chlorine* leciding for or against a water.

determination of the amount of chlorine is easily effected by of a solution of silver nitrate containing 4.79 grams per litre: of the water to be tested are placed in a beaker; a few drops of on of potassium chromate, enough to communicate a distinctly tinge, are added; the reaction is determined, and, if necessary, ture is rendered *faintly* alkaline by the addition of a solution of carbonate. The silver solution is now allowed to flow in, drop , from a burette, the fluid in the beaker being constantly stirred, e white precipitate assumes a *faint* reddish tinge. At this time ling of the burette is taken; each cubic centimetre of silver solu- ded represents 0.001 gram chlorine in 100 c.c. of water, or 0.01

rth — Organic matter.—Although the presence in a water of or- ubstances, *i. e.*, substances into whose composition carbon enters ement, cannot be considered as condemnatory, there is no reason bting that the most serious of contaminations of potable waters e caused by the presence of organic matters containing nitrogen, m the putrescible nature of these substances, and from the in- afforded by their presence of the existence in the water of excreta, as well as the presence under suitable conditions of the of the disease, be they germs or poisons. Every potable water small quantities of organic matter of vegetable origin, which are gnificance, provided the quantity be small and the water be taken iver, lake, or other body of moving water. If, however, a well- r other still water, contain much vegetable organic matter (its le nature being indicated by the absence or deficiency of chlorides), ce is to be condemned for that reason alone.

much more serious organic contamination is with nitrogenous of animal origin. Although our knowledge of the nature of the s of decomposition of these substances is still quite crude, it is hat among them are substances having a pronounced tendency ce low forms of fever, and to render those subjected to their in- eady victims to epidemic disorders. Whatever ill effects may om the use of waters polluted by the excreta of *healthy* individ- evil becomes much more serious during the prevalence of certain . There can remain no doubt that cholera and typhoid are trans- largely, if not exclusively, by the use of water into which the of a sufferer from the disease have found their way.

investigations of Mr. J. N. Radcliffe, on the cholera in London have shown that the disease was sharply limited to those por- the metropolis supplied with water from the Old Ford reservoirs East London Water Company, the earliest unquestionable out- f the disease having appeared within half a mile of these reser- In a subsequent report Dr. Buchanan traced the source of the c of typhoid, which occurred at Guildford, directly to contamina- water-supply. The town is supplied with a double system of high

port of the Medical Officer of the Privy Council, 1866 (9th), p. 295–331.

and low distribution, and with very few exceptions the disease was limited to those using the high service.* In the same year epidemics of typhoid occurred also at Winterton and at Terling; in both instances they were distinctly referable to contamination of the water with sewage.† Similar conclusions have been arrived at in investigations of the causes of many other epidemics.

Several processes have been devised for the determination of the amount of organic matter present in drinking-water; of these some are very readily applied, and are inaccurate in proportion to their facility. Probably the method best adapted to use by the practitioner in an emergency is that which has the least claim to exactness of results. This consists in simply partially filling a clean bottle with the water to be tested, and, after strong agitation, inhaling the air of the bottle through the nostrils. The presence or absence of an injurious amount of organic matter is inferred from the presence or absence of a disagreeable odor, however faint, of the inhaled air. The only advantage of this method is the facility of its application; it is exceedingly rough, and should be used only when time presses.

Another method is the permanganate test, which must be mentioned here that it may be avoided, especially as it has received a quasi-official indorsement at the hands of the New York Board of Health. In the report of that body for 1873,‡ directions are given for testing water by dropping into it a solution of potassium permanganate and by the discharge of color determining not only the presence, but also the amount of organic matter in the water. Drs. Frankland, Wanklyn, and Fox have clearly shown that the process is vitiated by both plus and minus errors. Any substance capable of abstracting oxygen from the permanganate will effect its decolorization, whether the substance be organic or not. On the other hand, in the conditions under which the test is applied, organic substances of an albuminoid nature and urea are not readily oxidized by permanganate. By the use of this test, therefor, a water may be condemned which contains a very small amount of organic matter while a water highly charged with impurities of the worst type would be passed without suspicion.

There are at present but two methods for the determination of organic matter in potable water which are worthy of serious consideration. These are Frankland and Armstrong's process, and Wanklyn's process. Frankland and Armstrong's method § is one which can only be applied in a fully appointed laboratory, and which, even under the most favorable conditions, is open to the serious objection that, owing to the small quantities to be determined and to the nature of the process, the experimental error may represent a quantity greater than that of the substance to be determined.

The process which is now almost exclusively used by chemists is that first suggested by Wanklyn, Chapman, and Smith, in 1867,‖ and is based upon the following reactions: 1st, the Nessler test for ammonia; *i. e.*, the production of a yellow color by ammonia in a saturated alkaline solution of mercuric iodide in potassium iodide; and 2d, the decomposition of organic nitrogenous substances, with production of ammonia,

* Report of Medical Officer of the Privy Council, 1867 (10th), p. 34.
† Dr. R. T. Thorne, ib., pp. 28, 41. ‡ p. 574.
§ Journ. Ch. Soc., N. S., vi., 77.
‖ Ibid., v., 448; id. vi., 152, 161. Wanklyn: Water Analysis, 3d ed. 3, 2. Fox: Water Analysis, 15.

when they are boiled with a highly alkaline solution of potassium permanganate.

For the application of this test, the following solutions are required:

a. Alkaline solution of potassium permanganate, made by dissolving 200 grams of potassium hydrate and 8 grams of potassium permanganate in a litre of water; the solution is boiled down to about 725 c.c., cooled, and brought to its original bulk by the addition of the requisite quantity of boiled distilled water.

b. Nessler reagent.—To prepare this, 35 grams of potassium iodide and 13 grams of mercuric chloride are dissolved in 800 c.c. of water, by the aid of heat and agitation. A cold saturated solution of mercuric chloride is then added, drop by drop, until the red precipitate which is formed is no longer redissolved on agitating the liquid; 160 grams of potassium hydrate are then dissolved in the liquid, to which, finally, a slight excess of mercuric chloride solution is added, and the bulk made up to one litre by the addition of water. The solution is then set aside until the red precipitate has subsided, when the clear, faintly yellowish liquid is decanted and preserved in well-stoppered bottles, which should not be too large and should be completely filled.

The glass stoppers of the bottles containing *a* and *b* should be well coated with paraffine, to prevent adhesion.

c. Standard solutions of ammonia.—These are a stronger and a weaker. The first is made by dissolving 3.15 grams of ammonium chloride in a litre of water; the second, by mixing 1 volume of the first with 99 volumes of distilled water. The weaker solution, which contains 0.00001 gram ($\frac{1}{100}$ milligram) of ammonia (NH_3) in each cubic centimetre, is the one which is used in examinations of water, the more concentrated solution serving simply for the convenient preparation of the other.

d. A saturated solution of sodium carbonate.

e. Distilled water.—The middle third of the distillate; 100 c.c. of which in a cylinder should not be perceptibly colored in ten minutes by the addition of 2 c.c. of Nessler reagent.

The testing of a water is conducted as follows: half a litre of the water to be tested (it is scarcely necessary to state that, before taking the sample, the demijohn or other vessel containing the water must be thoroughly shaken) is introduced, by a funnel, into a tubulated retort capable of holding one litre. If the water be acid, which is rarely the case, 10 c.c. of the solution of sodium carbonate *d* are added. Having connected the retort with a Liebig's condenser, the joint being made tight by a packing of moistened filter-paper, the water is made to boil as soon as possible by applying the flame of a Bunsen burner, brought close to the bottom of the naked retort (there is but little danger of fracture if the flame do not reach above the level of liquid inside). The first 50 c.c. of distillate are collected in a cylindrical vessel of clear glass, about an inch in diameter. The following 150 c.c. are collected and thrown away, after which the fire is withdrawn. While these are passing over, the first 50 c.c. are Nesslerized (*vide infra*), and the result, plus one-third as much again, is the amount of free ammonia contained in the half-litre of water.

When 200 c.c. have distilled over, all the free ammonia has been removed, and it now remains to decompose the organic material, and determine the amount of ammonia formed. To effect this, 50 c.c. of the permanganate solution *a* are added through the funnel to the contents of the retort, which is shaken, stoppered, and again heated. The dis-

tillate is now collected in separate portions of 50 c.c. each, in glass cylinders, until three such portions have been collected. These are then separately Nesslerized as follows: 2 c.c. of the Nessler reagent are added to the sample of 50 c.c. of distillate; if ammonia be present, a yellow or brown color will be produced, dark in proportion to the quantity of ammonia present. Into another cylinder a given quantity of the standard solution of ammonia *c* is allowed to flow from a burette; enough water is added to make the bulk up to 50 c.c., and then 2 c.c. of Nessler reagent. This cylinder, and that containing the 50 c.c. of Nesslerized distillate, are then placed side by side upon a sheet of white paper and their color examined. If the shade of color in the two cylinders be *exactly* the same, the 50 c.c. of distillate contain the same amount of ammonia as the quantity of standard solution of ammonia used. If the colors be different in intensity, another comparison-cylinder must be arranged, using more or less of the standard solution, as the first comparison-cylinder was lighter or darker than the distillate. When the proper similarity of shades has been attained, the number of cubic centimetres of the standard solution used is determined by the reading on the burette. This process, which, with a little practice, is neither difficult nor tedious, is to be repeated with the first 50 c.c. of distillate and with the three portions of 50 c.c. each, distilled after the addition of the permanganate solution. If, for example, it required 1 c.c. of standard solution in Nesslerizing the first 50 c.c., and for the others 3.5 c.c., 1.5 c.c., and 0.2 c.c., the following is the result and the usual method of recording it:

Free ammonia	.01	milligr.
Correction	.003	milligr.
	.013	milligr.
Free ammonia per litre		.026 milligr.
Albuminoid ammonia	.035	milligr.
Albuminoid ammonia	.015	milligr.
Albuminoid ammonia	.002	milligr.
	.052	milligr.
Albuminoid ammonia, per litre		.104 milligr.

Concerning the deductions to be drawn from the determination of ammonia, Mr. Wanklyn* says: "If a water yield 0.00 parts of albuminoid ammonia per million, it may be passed as organically pure, despite of much free ammonia and chlorides; and if, indeed, the albuminoid ammonia amount to .02, or to less than 0.05 part per million,† the water belongs to the class of very pure water. When the albuminoid ammonia amounts to .05, then the proportion of free ammonia becomes an element in the calculation; and I should be inclined to regard with some suspicion a water yielding a considerable quantity of free ammonia along with .05 part of albuminoid ammonia per million. Free ammonia, however, being absent or very small, a water should not be condemned unless the albuminoid ammonia reaches something like 0.10 per million. Albu-

* Water Analysis, 3d ed., 51.

† Milligrams per litre.

minoid ammonia above 0.10 per million begins to be a very suspicious sign, and over 0.15 ought to condemn a water absolutely. The absence of chlorine, or the absence of more than one grain of chlorine per gallon, is a sign that the organic impurity is of vegetable rather than animal origin; but it would be a great mistake to allow water highly contaminated with vegetable matter to be taken for domestic use."

Fifth—Nitrates.—The existence and quantity of alkaline nitrates in water were formerly regarded as of much greater importance than that now accorded. They were considered as indicating, if not the actual sewage present, at least the amount of previous contamination, for the reason that they are the principal ultimate products of the oxidation of nitrogen contained in organic substances. They exist, however, also in waters perfectly free from organic contamination as well as in rain-water, being taken up by the former in its passage through certain geological strata, and being formed in the latter probably by direct union of the nitrogen and oxygen of the air.

Sixth—Poisonous metals.—The metals most liable to occur in potable waters are iron, copper, and lead.

α. Iron may be dissolved by water either during its passage through ferruginous strata in the earth, or by conduction through iron pipes. Certain ferruginous waters are valuable medicinal agents, and may contain as much as 607 milligrams of salts of iron to the litre. For ordinary uses, however, a water should not contain more than three milligrams per litre of iron. The amount of iron dissolved by water in passing through iron pipes is exceedingly small. The distribution of water in large cities, and frequently the main supply also, is through such channels.

Mr. A. W. Blyth has also shown that water containing organic matter is purified, to a large extent, of these contaminations by passage through iron pipes.

β. Copper.—Drinking-water is not liable to become contaminated with the salts of this element except when it comes in contact with deposits of the metal, or of its ores in its passage through the earth. The experiments of Muir have shown that pure water would not dissolve copper, but that water containing carbon dioxide, especially when also containing calcium chloride and ammonium nitrate, would dissolve it in considerable quantity.

γ. Lead.—The most serious, as well as the most common metallic contamination of water, is that with lead. Although a water contain a very small quantity of lead salts, there is no doubt that its continued use will produce well-marked cases of chronic lead-poisoning, and numerous instances are recorded in which the disorder has been traced directly to this cause, and has ceased with its removal.

The power possessed by a water of dissolving lead varies materially with the nature of the substances which it holds in solution. The presence of nitrates is favorable to the solution of lead, an influence which is, however, much diminished by the simultaneous presence of other salts. A water highly charged with oxygen dissolves lead readily, especially if the metallic surface be so exposed to the action of the water as to be alternately acted upon by it and by the air. On the other hand, waters containing carbonates or free carbonic acid may be left in contact with lead with comparative impunity, owing to the formation of a protective coating of the insoluble carbonate of lead on the surface of the metal. This does not apply, however, to water charged with a large excess of carbon dioxide under pressure. It will be observed from what precedes

that of all natural waters that most liable to contamination with lead is rain-water; it contains ammonium nitrate with very small quantities of other salts; and it is highly aërated, but contains no carbonates and comparatively small quantities of carbon dioxide. Obviously, therefor, rain-water should neither be collected from a leaden roof, nor stored in leaden tanks, nor drank after having been long in contact with lead pipes. As a rule, the purer the water the more liable it is to dissolve lead when brought in contact with that metal, especially if the contact occur when the water is at a high temperature, or when it lasts for a long period.

It has been proposed, in order to avoid the solution of lead, to use pipes of lead coated internally with block tin. Unfortunately, however, it has been found that wherever a fault occurred in the coating, the lead is dissolved much more rapidly than from pipes made entirely of lead. Moreover, tin is a substance which is by no means insoluble in water, its solubility being materially increased when it is alloyed with even a very small proportion of lead.

To determine the power of water for dissolving lead, take two tumblers of the water to be tested; in one place a piece of lead, whose surface has been scraped bright, and allow them to stand twenty-four hours. At the end of that time remove the lead and pass sulphuretted hydrogen through the water in both tumblers; if the one which contained the metal become perceptibly darker than the other, the water has a power of dissolving lead such as to render its contact with surfaces of that metal dangerous if prolonged beyond a short time.

The testing of water for poisonous metals is a very simple matter, and consists in adding to the water, in a porcelain capsule, some solution of ammonium sulphydrate. If the water become perceptibly darker after the addition of the reagent, it contains a poisonous metal, whose nature is then to be determined. Having determined whether the metal is iron, copper, or lead, a quantitative determination may be made by imitating the shade of color produced by ammonium sulphydrate in a given bulk of the water, with a standard solution of a salt of the corresponding metal and ammonium sulphydrate; the volume of the standard solution used containing the same amount of the metal as the volume of water tested. The standard solutions are the following: for iron, 4.96 grams of ferrous sulphate dissolved in 1 litre of water; each cubic centimetre contains 0.001 gram iron. For copper, 3.93 grams of cupric sulphate dissolved in 1 litre of water; each cubic centimetre contains 0.001 gram copper. For lead, 1.66 gram of lead acetate in 1 litre of water; each cubic centimetre contains 0.001 gram lead.

Seventh—Suspended solids.—Most natural waters deposit, on standing, more or less solid insoluble material. These substances have been either suspended mechanically in the water, which deposits them when it remains at rest, or they have been in solution and are deposited by becoming insoluble as the water is deprived of carbon dioxide by exposure to air and by relief from pressure.

The suspended particles should be collected by subsidence in a conical glass, and should be examined microscopically for low forms of animal and vegetable life. The quantity of suspended solids is determined by passing a litre of the turbid water through a dried and weighed filter, which, with the collected deposit, is again dried and weighed. The difference between the two weights is the weight of suspended matter in a litre of the water.

Purification of water.—The artificial means of rendering a more or

less contaminated water fit for use are of five kinds: 1. Distillation; 2. Subsidence; 3. Filtration; 4. Precipitation; 5. Boiling.

The method by *distillation* is used in the laboratory when a very pure water is desired, and also at sea upon steamships, and even on sailing vessels upon occasion. Distilled water is, however, too pure for continued use, being hard of digestion, and flat to the taste from the absence of gases and of solid matter in solution. When circumstances oblige the use of such water, it should be agitated with air, and should be charged with inorganic matter to the extent of about 0.15 gram each of calcic bicarbonate and sodium chloride to the litre.

Purification by *subsidence* is adopted only as an adjunct to precipitation and filtration, and for the separation of the heavier particles of suspended matter.

The ideal process of *filtration* consists in the separation of all particles of suspended matter, without any alteration of such substances as are held in solution. In the filtration of potable waters on a large scale, however, the more minute particles of suspended matters are only partially separated, while, on the other hand, an important change in the dissolved materials takes place, at least in certain kinds of filters, in the oxidation of organic matters, whether in solution or in suspension. In the filtration of large quantities of water it is passed through sand or charcoal, or through both substances arranged in alternate layers. Filtration through charcoal is much more effective than that through sand, owing to the much greater activity of the oxidation of nitrogenized organic matter in the former case.

Precipitation processes are only adapted to hard waters, and are designed to separate the excess of calcium salt, and at the same time a considerable quantity of organic matter, which is mechanically carried down with the precipitate. The method usually followed consists in the addition of lime (in the form of lime-water), in just sufficient quantity to neutralize the excess of carbon dioxide present in the water. The added lime, together with the calcium salt naturally present in the water, is then precipitated, except that small portion of calcium carbonate which the water, freed of carbon dioxide, is capable of dissolving. To determine when sufficient lime-water has been added, take a sample from time to time during the addition, and test it with solution of silver nitrate until a brown precipitate is formed. At this point cease the addition of lime-water and mix the limed water with further portions of the hard water, until a sample, treated with silver-nitrate solution, gives a yellowish in place of a brown color. The purification of water by *boiling* can only be carried on upon a small scale; it is, however, of great value for the softening of temporarily hard waters, and for the destruction of organized impurities, for which latter purpose it should never be neglected during outbreaks of cholera and typhoid, if, indeed, water be drank at all at such times.

Mineral Waters.

Under this head are classed waters charged to such an extent with dissolved substances, or having a temperature such as to render them available for therapeutical uses. As a rule, spring-water has a temperature less than 15°, but there are many springs whose waters are much warmer. When their temperature is higher than 20° they are known as thermal

springs, and are frequently of therapeutical value independently of the nature of their dissolved solids, which is exceedingly various. Among the most noted thermal springs are those of Wildbad, 35.5° ; Warmbrunn, 38° ; Töplitz, 49° ; Buxton, 28° ; Clifton, 30° ; Chaudes-Aigues, 81° ; Ems, 46° ; Carlsbad, 73° ; Arkansas Hot Springs from 40.5° to 66° ; Virginia Hot Springs, 37.8° to 41°. The water of the great Geyser in Iceland has a temperature of over 100° in the centre.

The composition of mineral waters varies greatly, according to the nature of the strata or veins through which the water passes, and to the conditions of pressure and previous composition under which it is in contact with these deposits. Waters of very different composition in some localities come to the surface in close proximity to each other, as at Saratoga Springs, where the Congress and Columbian springs, differing widely from each other in their chemical and therapeutical properties, are only a few rods apart.

The substances almost universally present in mineral waters are: oxygen, nitrogen, carbon dioxide, sodium carbonate, bicarbonate, sulphate and chloride, calcium carbonate and bicarbonate. Of substances occasionally present the most important are: sulphydric acid, sulphides of sodium, iron and magnesium, bromides and iodides of sodium and magnesium, calcium and magnesium chlorides, carbonate, bicarbonate, sulphate, peroxide and crenate of iron, silicates of sodium, calcium, magnesium and iron, aluminium salts, salts of lithium, cæsium and rubidium, free sulphuric, silicic, arsenic and boric acids, and ammoniacal salts.

Although a sharply defined classification of mineral waters is not possible, one which is useful, if not accurate, may be made, based upon the predominance of some constituent or constituents which impart to the water a well-defined therapeutic value. A classification which has been generally adopted is into five classes:

First—Acidulous waters, those whose value depends upon the presence of carbon dioxide.

Second—Alkaline waters, those containing a notable proportion of carbonates, or bicarbonates of sodium, potassium, or lithium.

Third—Chalybeate waters, those charged with compounds of iron.

Fourth—Saline waters, those containing neutral salts in considerable quantity.

Fifth—Sulphurous waters, those holding hydrogen sulphide, or a metallic sulphide in solution.

Besides those waters which may be classed under one of the above heads, there are others which, containing some active substance not usually present in natural waters, such as alum, free sulphuric acid, or arsenical compounds, may for the present be placed in a sixth class.

Acidulous waters.—These waters, of which the artificially prepared *carbonic water*, or *soda-water*, may be considered the type, contain but small quantities of solid matters in solution, the most abundant being the bicarbonates of sodium and of calcium, and sodium chloride. They are always cool, fresh, and sparkling, owing to the presence in them of carbon dioxide in considerable quantity, and to the absence of hydrogen or other sulphides.

Alkaline waters.—The temperature of waters of this class is usually above 20°, although some are cooler. They are alkaline in reaction, some sufficiently so to have a soapy taste, others only after expulsion of the free carbon dioxide, which they contain in very variable proportion. Their principal solid constituents are the bicarbonates of sodium, calcium,

magnesium, and sometimes lithium. Their tenure in sodium chloride is usually less than that of the acidulous waters.

Chalybeate waters.—Iron, being widely distributed in nature, is contained in most natural waters, fresh or mineral. When the quantity of iron salts exceeds forty milligrams per litre, the water may be considered as having medicinal value. Chalybeate waters are usually cool, sometimes warm, have a ferruginous taste, and are clear as they emerge from the earth. Those containing iron in the form of its bicarbonate become turbid and deposit a brownish yellow sediment on exposure to air, the bicarbonate being decomposed and carbon dioxide given off. Besides ferrous bicarbonate, many of the waters of this class contain ferrous sulphate, crenate and apocrenate, calcium carbonate, sulphates of potassium, sodium, calcium, magnesium, and aluminium, notable quantities of sodium chloride, and sometimes arsenical compounds.

Saline waters.—The solid constituents of waters of this class are so diverse in kind that the group may well be divided in subgroups.

α. *Chlorine waters* are such as contain large quantities of sodium chloride, associated with less amounts of the chlorides of potassium, calcium, and magnesium. Some of these are so rich in sodium chloride that they are not of service as therapeutic agents, but are evaporated either by solar or artificial heat, to yield a more or less pure salt. Any natural water containing more than 3 grams per litre of sodium chloride belongs to this class, provided it do not contain substances more active in their medicinal action in such proportion as to warrant its classification elsewhere. Waters containing more than 15 grams per litre are too concentrated for internal administration. They are usually cool, and have a salt, but not a bitter taste. Some of them are highly charged with carbon dioxide, and in some instances the pressure under which they are discharged from the earth is sufficient to project them to a height of over thirty feet. They contain also traces of iodides and bromides, and bicarbonates of sodium and calcium.

β. *Sulphate waters* are actively purgative from the presence of considerable proportions of the sulphates of sodium, calcium, and magnesium. Some contain large quantities of sodium sulphate, with mere traces of the calcium and magnesium salts, while in others the proportion of the sulphates of magnesium and calcium is as high as 30 grams per litre, to 20 grams per litre of sodium sulphate. They vary much in concentration; from 5 grams of total solids to the litre in some, to near 60 grams per litre in others. They have a salty, bitter taste, and vary much in temperature.

γ. *Bromine and iodine waters* are such as contain the bromides or iodides of potassium, sodium, or magnesium in sufficient quantity to communicate to them the medicinal properties of those salts. An exaggerated type of this class is to be found in the water of the Dead Sea, which contains a large proportion of magnesium bromide. The mineral waters of Pomeroy, O., are worked as a source of bromine.

Sulphurous waters.—The waters of this class are distinguished by the presence of hydrogen sulphide or of the sulphides of the alkaline metals—usually of both. Their temperature varies much in different waters, but is usually high. They have the disagreeable odor of hydrogen sulphide, and form a black mixture with a solution of a lead salt. The fixed salts which they hold in solution are principally sodium chloride, sulphate, and bicarbonate, and calcium bicarbonate. The proportion of total solids varies in different waters of this class from 0.2 to 4 grams per litre.

COMPOSITION OF MINERAL WATERS.

QUANTITIES IN MILLIGRAMS PER LITRE.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
	Niederselters.	Soultzmatt.	Condillac.	Wilhelms Quelle.	Apollinaris.	Rhens.	Vichy (Grande Grille).	Vichy (Hôpital).	Vichy (Célestins).	Plombières (Dames)
Temperature	17.5°	11°	13°	13.5°	18.5°	10.5°	41.8°	30.8°	....	....
Density	1.0084	1.0018	....	....	....	1.0031	....	....	....	....
Total solids	4070	2091	2193	2457	....	4345	7006	7155	7195	240
Carbon dioxide	1035	1946	1083	2249	....	2458	908	1067	1049	12.6
Sodium bicarbonate	979	957	166	84	1257*	1049	4883	5029	5103	11
Potassium "	....	....	....	....	....	59	352	440	315	1.3
Lithium "	....	20	....	3	....	....	....	....	....	....
Calcium "	551	431	1359	677	59*	577	434	570	462	38
Strontium "	traces.	....	....	3	....	....	3	5	5	....
Barium "	....	....	....	....	....	....	....	....	....	....
Magnesium "	209	313	35	167	442*	405	303	200	328	6.7
Ferrous "	30	....	....	5	....	4	4	4	4	....
Manganous "	....	....	....	2	....	....	traces.	traces.	traces.	....
Sodium chloride	2040	71	150	1690	466	1267	534	518	534	6.7
Potassium "	1	....	....	37	....	....	....	....	....	....
Lithium "	....	....	....	....	....	....	....	....	....	....
Calcium "	....	....	....	....	....	....	....	....	....	....
Magnesium chloride	....	....	....	....	....	....	....	....	....	....
Sodium sulphate	150	23	175	....	300	972	291	291	291	92.7
Potassium "	....	148	....	23	....	....	....	....	....	....
Magnesium "	....	....	....	....	....	....	....	....	....	....
Calcium "	....	....	53	....	....	....	....	....	....	....
Sodium phosphate	40	....	....	1	....	....	130	46	91	....
Potassium "	....	....	....	....	....	....	....	....	....	....
Calcium "	....	....	....	....	....	....	....	....	....	....
Aluminium "	....	....	....	....	....	....	....	....	....	....
Sodium iodide	....	....	....	....	....	....	....	....	....	....
Potassium "	....	....	traces.	....	....	....	....	....	....	....
Sodium bromide	traces.	....	....	1	....	....	....	....	....	....
Potassium "	....	....	....	....	....	....	....	....	....	....
Alumina	50	....	....	....	....	....	....	....	....	....
Silex		63	....	101	8	10	70	50	60	....
Organic matter	traces.	....	....	....	....	....	traces.	traces.	traces.	traces.
Ferrous sulphate	....	....	....	....	....	....	....	....	....	....
Ferrous crenate	....	....	10	....	....	....	....	....	....	....
	O. Henry.	Béchamp.	O. Henry.	Frezenius.	Bischof.	Mohr.	Bouquet.	Bouquet.	Bouquet.	Jutier and Lefort.

* Calculated as carbonates instead of bicarbonates.

(1.) Sodium and calcium crenates, traces. (2.) Sodium borate, 65. (3.) Silicates of calcium and of aluminium, 245. (4.) Oxide of iron, 20. (5.) Alumina, strontia, lithia, organic matter—traces. (7, 8, and 9.) Sodium arsenate, 2; sodium borate, traces. (10.) Calcium fluoride, 9.2; sodium silicate, 57; lithium silicate, traces; baregine, traces.

COMPOSITION OF MINERAL WATERS—*Continued.*

	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
	Ems (Fürstenbrunnen).	Ems (Kesselbrunnen).	Buffalo (Lithia).	Gettysburg.	Ballston (Artesian).	Ballston (Sans Souci).	Glen Flora, Wis.	Bethesda.	Cheltenham (Royal Old Well).	Niedertrenn.
Temperature	35.3°	46.3°	....	....	11.1°	10°	....	....	....	....
Density	1.0031	1.0031	....	....	1.0159	1.015	....	....	....	....
Total solids	3543	3518	1405	3803	21138	16906	606	612	....	4628
Carbon dioxide	902	884	417	....	3627	4580	....	....	....	19
Sodium bicarbonate	2032	1979	....	658	204	82	111	22	....	....
Potassium "	....	....	606	....	....	....	....	....	....	....
Lithium "	traces.	traces.	32	....	133	202	....	....	....	....
Calcium "	233	236	214	1157	4082	3311	267	292	243*	179*
Strontium "	0.28	0.48	....	....	15	traces.	....	....	....	....
Barium "	....	....	25	....	67	31	....	....	....	....
Magnesium "	200	187	....	1086	3096	3104	190	212	97*	6.5*
Ferrous "	2.6	3.6	4.3	....	27	158	2	1	....	10.3*
Manganous "	0.8	0.6	....	....	....	....	....	....	....	....
Sodium chloride	984	1012	70	....	12855	9809	3	20	3420	3089
Potassium "	....	....	....	traces.	570	97	....	....	....	139
Lithium "	....	....	....	....	....	....	....	....	....	4.8
Calcium "	....	....	....	....	....	....	....	....	....	794
Magnesium "	....	....	....	....	....	....	....	....	114	312
Sodium sulphate	2.2	0.8	....	....	....	....	32	9	1354	....
Potassium "	39	51	....	....	9	....	....	8	....	....
Magnesium "	....	....	12.7	....	....	....	....	...	....	....
Calcium "	....	....	472	760	....	....	....	....	....	....
Sodium phosphate	....	....	....	....	1	....	....	traces.	....	....
Potassium "	....	....	....	traces.	....	....	....	....	....	....
Calcium "	....	....	....	....	....	54	....	....	....	....
Aluminium "	0.4	0.1	....	....	....	....	....	....	....	....
Sodium iodide	traces.	traces.	....	....	2	11	....	....	....	74
Potassium "	....	....	....	....	....	....	....	....	....	....
Sodium bromide	....	....	....	....	62	18	....	....	....	10.7
Potassium "	....	....	....	....	....	....	....	....	....	....
Alumina	....	....	....	....	1.3	trace.	4	2	....	traces.
Silex	....	....	27	143	13	20	16	11	38	1
Organic matter	....	....	traces.	....	traces.	....	2	34	257	....
Ferrous sulphate	....	....	....	....	....	....	....	....	....	....
Ferrous crenate	....	....	....	....	....	....	....	....	....	....
	Frezenius.	Frezenius.	Tonry.	Mayer.	Chandler.	Perkins.	Blaney.	Blaney.	Abel and Rowney.	-

* Calculated as carbonates instead of bicarbonates.

(13.) Aluminium sulphate, 129; phosphoric acid and iodine, traces. (16.) Rubidium chloride, trace. (20.) Ammonium chloride, trace; peroxide of iron, 15.

COMPOSITION OF MINERAL WATERS—*Continued.*

21.	22.	23.	24.	25.	26.	27.	28.	29.	30.	
Homburg (Elizabeth).	Homburg (Louis).	Kissingen (Rakoczy).	Saratoga (Congress).	Saratoga (Empire).	Saratoga (Hathorn).	Saratoga (Geyser).	Saratogn (Excelsior).	Wankegan.	Poland.	
10°	10°	11°	....	....	....	7.8°	....	....	....	Temperature.
1.0015	1.012	1.0073	....	....	1.009	1.011	....	....	....	Density.
14175	14681	8735	7603	11662	15128	16995	8823	837	66	Total solids.
2810	2399	1632	3340	2914	3252	3865	2127	....	....	Carbon dioxide.
....	....	....	184	155	74	1223	257*	....	2*	Sodium bicarbonate
....	....	....	....	....	....	....	....	....	....	Potassium "
....	....	....	82	36	196	154	....	....	traces.	Lithium "
1431*	1275*	1061*	2458	1880	2925	2886	1319*	266	23*	Calcium "
....	....	....	traces.	traces.	traces.	7	....	....	....	Strontium "
....	....	....	16	1.3	30	35	....	....	....	Barium "
262*	6*	17*	2085	736	3025	2560	554*	296	5*	Magnesium "
60*	51*	31.6*	6	14	29	17	55*	2	traces.	Ferrous "
....	....	traces.	....	....	....	....	....	....	....	Manganous "
10306	10997	5882	6864	8684	8741	9634	4953	32	8	Sodium chloride.
....	287	287	138	74	165	422	....	traces.	....	Potassium "
....	....	200	....	....	....	....	....	....	....	Lithium "
1010	1238	....	....	....	....	....	....	....	....	Calcium "
1014	781	303	....	....	....	....	....	....	....	Magnesium "
49.6	....	....	....	....	....	....	23	99	....	Sodium sulphate.
....	....	....	15	47	....	6	....	....	3	Potassium "
....	....	587	....	....	....	....	....	....	....	Magnesium "
....	29	389	....	....	....	....	....	127	....	Calcium "
....	....	....	0.3	0.4	traces.	traces.	....	....	....	Sodium phosphate.
....	....	....	....	....	....	....	....	....	....	Potassium "
....	....	5.6	....	....	....	....	....	....	....	Calcium "
....	....	traces.	....	....	....	....	....	....	....	Aluminium "
traces.	traces.	traces.	2.4	0.1	3.4	4.3	73	....	....	Sodium iodide.
....	....	....	....	....	....	....	....	....	....	Potassium "
traces.	traces.	8.4	147	4.6	26	38	....	....	....	Sodium bromide.
....	....	....	....	....	....	....	traces.	....	....	Potassium "
....	traces.	traces.	traces.	7.2	2.2	traces.	....	4	traces.	Alumina.
41	16	13	14	20	22	11	....	6	18	Silex.
....	....	....	....	....	traces.	traces.	....	3	5	Organic matter.
....	....	....	....	....	....	....	....	....	....	Ferrous sulphate.
....	....	....	....	....	....	....	....	....	....	Ferrous crenate.
Liebig.	Liebig.	Liebig.	Chandler.	Chandler.	?	Chandler.	Allen.	Blaney.	Bartlett.	

* Calculated as carbonates instead of bicarbonates.

(23.) Strontium sulphate, sodium borate, calcium fluoride, traces; sodium nitrate, 9.3; ammonia, 0.9. (24.) Calcium fluoride and sodium borate, traces. (25.) Calcium fluoride and sodium borate, traces. (26.) Calcium fluoride and sodium borate, traces. (27.) Calcium fluoride and sodium borate, traces. (28.) Potassium silicate, 120; sodium silicate, 69; strontium sulphate, trace. (30.) Calcium fluoride and lithia, traces.

COMPOSITION OF MINERAL WATERS—*Continued.*

	31.	32.	33.	34.	35.	36.	37.	38.	39.	40.
	Carlsbad (Sprudel).	Marienbad (Kreuzbrunnen).	Pullna	Friedrichshall.	Ofner (Rakoczy).	Hunyadi Janos.	St. Leon.	Helibrunn.	Töplitz (Hauptquelle).	Bourbonne.
Temperature	73°	12	....	....	....	....	....	....	....	57.5°
Density	1.0047	1.007	....	....	1.0524	1.0031	1.0118	....	....	....
Total solids	5459	8653	32440	25294	57681	44879	14940	4710	4943	7471
Carbon dioxide	788	....	807	402	....	....	....	9	....	....
Sodium bicarbonate	1262	1154	....	....	434*	1166*	....	506*	2844*	....
Potassium "	....	....	....	....	....	....	....	....	....	....
Lithium "	....	6.3	....	....	....	....	....	....	18*	....
Calcium "	309	3.6	100	15	700*	....	505	54*	344*	98*
Strontium "	....	1.7	....	....	....	....	....	....	....	....
Barium "	....	....	....	....	....	....	....	....	....	....
Magnesium "	....	463	834	520	....	....	1408	25*	57*	....
Ferrous "	....	45.3	....	....	153*	....	12	....	39*	....
Manganous "	....	5	....	....	....	....	....	....	....	....
Sodium chloride	1038	1454	....	7956	2314	1676	11612	3928	458	5771
Potassium "	....	....	....	....	....	....	233	....	110	....
Lithium "	....	....	....	....	....	....	28	....	....	....
Calcium "	....	....	....	....	....	....	57	....	....	....
Magnesium "	....	....	2260	3939	....	....	1011	....	....	381
Sodium sulphate	2587	4756	16120	6056	20828	17927	....	48	....	....
Potassium "	....	65	625	198	67	158	....	....	459	129
Magnesium "	....	....	12121	5150	25037	22422	....	....	....	....
Calcium "	....	....	338	1346	6676	1512	1	....	....	879
Sodium phosphate	....	....	....	....	....	....	3	....	....	....
Potassium "	....	....	13.2	....	....	....	....	....	....	....
Calcium "	0.22	2.4	....	....	....	....	....	....	....	....
Aluminium "	0.32	7.1	....	....	....	....	....	....	23	....
Sodium iodide	....	....	....	....	....	....	4	98	60	....
Potassium "	....	....	....	....	....	....	....	....	....	....
Sodium bromide	....	traces.	....	....	7	....	14	32	....	64
Potassium "	....	....	....	....	....	....	....	....	....	....
Alumina	....	....	23	traces.	27	4	10	....	....	29
Silex	75	....		traces.	151	12	23	13	330	120
Organic matter	....	....	....	traces.	....	....	traces.	traces.	95	....
Ferrous sulphate	....	....	....	....	....	....	....	....	....	....
Ferrous crenate	....	....	....	....	....	....	....	....	....	....
	Berzelius.	Berzelius.	Struve.	Liebig.	Tichborn.	Ulex.	Chandler and Cairns.	Barmel.	Fichtus.	Mialhe and Figuier.

* Calculated as carbonates instead of bicarbonates.

(31.) Calcium fluoride, 3.2; ferric oxide, 3.6; manganese oxide, 0.8; magnesia, 179; strontia, 0.96. (32.) Calcium fluoride, traces. (33.) Lithium sulphate, 0.4; strontium sulphate, 2.8; barium sulphate, 0.1. (34.) Magnesium bromide, 11. (38.) Peroxide of iron, 8.

COMPOSITION OF MINERAL WATERS—*Continued.*

41.	42.	43.	44.	45.	46.	47.	4.	49.	50.	
Orezza.	Schwalbach.	Forges (Cardinale).	Passy.	Saratoga (Columbian).	Homburg (Stahlbrunnen).	Pyrmont.	Cheltenham.	Bedford (Alum).	Rockbridge (Alum).	
....	10.4°	....	....	....	....	....	....	....	....	Temperature.
....	1.0007	....	....	1.0073	....	....	....	....	....	Density.
849	603	270	5446	6981	14989	2944	4156	1215	801	Total solids.
2471	1920	445	traces.	2316	....	....	....	....	38	Carbon dioxide.
....	20.6	....	....	264	....	....	....	....	....	Sodium bicarbonate
....	....	....	....	....	....	....	....	....	....	Potassium "
....	....	....	....	....	....	....	....	....	....	Lithium "
602*	221	....	....	1166*	1076*	855*	159*	....	....	Calcium "
....	....	....	....	....	....	....	....	....	....	Strontium "
....	....	....	....	....	....	....	....	....	....	Barium "
74*	212	76	....	801	....	46*	....	....	....	Magnesium "
128*	84	....	....	96*	146*	70*	66*	....	....	Ferrous "
traces.	18.4	....	....	....	....	7*	....	....	....	Manganous "
6	7	12	358	4576	11404	....	2262	3	7	Sodium chloride.
....	....	....	....	....	....	....	....	....	....	Potassium "
....	....	....	....	....	....	....	....	....	....	Lithium "
....	....	....	....	....	1523	....	735	....	....	Calcium "
....	....	3	....	....	761	161	484	....	....	Magnesium "
....	7.8	6	....	....	....	306	....	15	....	Sodium sulphate.
....	3.7	....	....	....	25	6	....	12	....	Potassium "
....	....	....	597	....	....	385	....	216	19	Magnesium "
21	....	40	2344	....	21	1031	....	86	25	Calcium "
....	traces.	....	....	....	....	....	....	....	....	Sodium phosphate.
....	....	....	....	....	....	....	....	....	....	Potassium "
....	....	....	....	....	....	....	....	5	....	Calcium "
....	....	....	407	....	....	2	....	....	....	Aluminium "
....	....	....	....	35	....	....	....	....	....	Sodium iodide.
....	....	....	....	....	....	....	....	....	....	Potassium "
....	....	....	....	....	....	....	....	....	....	Sodium bromide.
....	....	....	....	....	....	....	....	....	....	Potassium "
traces.	....	33	....	....	....	....	....	....	252	Alumina.
4	32	....	....	35	45	71	20	29	....	Silex.
....	traces.	....	traces.	....	....	....	40	5	....	Organic matter.
....	....	....	607	....	....	....	428	11	....	Ferrous sulphate.
....	....	98	....	....	....	....	....	....	....	Ferrous crenate.
Poggiale.	Frezenius.	O. Henry.	Deyeux and Barruel.	Emmons.	Liebig.	Struve.	Hofmann.	Hardin.	A. A. Hayes	

* Calculated as carbonates instead of bicarbonates.

(43.) Crenates of sodium and potassium, 2. (44.) Alum, 407. (49.) Sulphates of copper, zinc, cobalt, and nickel, 4.11; ferric sulphate, 330; aluminium sulphate, 414; manganese sulphate, 3.29; lithium sulphate, 4.14; sulphuric acid (free), 68.85; magnesium and ammonium nitrates, 8.82.

COMPOSITION OF MINERAL WATERS—*Continued.*

	51.	52.	53.	54.	55.	56.	57.	58.	59.	60.
	Bagnères (Bayen).	Vernet (Mercador).	Aix-la-Chapelle (Cornelius).	Aix-la-Chapelle (Empereur).	Aix (Savoy).	Massena (St. Regis).	Roanoke (Red Sulphur).	Mercer Co., Virginia.	White Sulphur, Virginia.	Red Sulphur, Virginia.
Temperature	68°	....	45.4°	55°	45°	....	....	....	....	48°
Density	....	....	....	....	....	1.0317	....	1.0065	1.0025	....
Total solids	227	267	3730	4102	430	3404	372	2578	2314	465
Carbon dioxide	....	....	....	....	26	....	....	....	92	54
Sodium bicarbonate	traces.	105*	497*	650*	....	....	....	....	....	....
Potassium "	....	9.3*	....	....	....	....	....	....	....	....
Lithium "	....	....	0.29*	0.29*	....	....	0.27*	....	....	....
Calcium "	....	traces.	132*	158*	148*	83	112*	....	121*	90*
Strontium "	....	....	traces.	traces.	traces.	....	....	....	....	....
Barium "	....	....	....	....	....	....	....	....	....	....
Magnesium "	....	traces.	25*	51*	26*	....	100*	....	....	83*
Ferrous "	....	....	6*	10*	9*	8	0.99*	....	....	....
Manganous "	....	....	....	....	....	....	0.27*	....	....	....
Sodium chloride	83	15	2465	2639	8	1368	4	34	....	....
Potassium "	....	....	....	....	....	8	....	....	....	....
Lithium "	....	....	....	....	....	....	....	....	....	....
Calcium "	....	....	....	....	....	....	....	....	....	....
Magnesium "	....	....	....	....	17	513	....	....	17	....
Sodium sulphate	traces.	18	287	288	96	60	52	10	....	71
Potassium "	traces.	....	107	154	....	....	6	33	....	....
Magnesium "	....	....	....	....	35	....	....	105	607	....
Calcium "	traces.	traces.	....	....	16	1041	38	....	1343	10
Sodium phosphate	....	....	....	....	....	22	....	....	....	....
Potassium "	....	....	....	....	....	....	....	....	....	....
Calcium "	....	....	....	....	....	....	0.5	....	....	....
Aluminium "	....	....	traces.	traces.	traces.	....	....	....	....	....
Sodium iodide	traces.	....	....	....	traces.	....	....	....	....	....
Potassium "	....	....	....	....	....	....	....	....	....	....
Sodium bromide	....	....	4	4	....	....	....	....	....	....
Potassium "	....	....	....	....	....	....	....	....	....	....
Alumina	....	10	....	....	....	....	0.11	....	....	....
Silex	44	49	60	66	....	....	14	83	27	2
Organic matter	traces.	....	93	75	....	....	13	59	75	....
Ferrous sulphate	....	....	....	....	....	....	....	1173	....	....
Ferrous crenate	....	....	....	....	....	....	....	....	....	....
	Fhol.	Bouis.	Liebig.	Liebig.	Liebig.	Mayer.	Hardin.	Dana Hayes.	A. A. Hayes	A. A. Hayes

* Calculated as carbonates instead of bicarbonates.

(51.) Sodium sulphide, 78; ferrous and magnesium sulphides, traces; calcium silicate, 22. (52.) Sodium sulphide, 41; oxides of iron and aluminium, 10. (53.) Sodium sulphide, 19.5. (55.) Hydrogen sulphide, 26.8 c.c.; aluminium sulphate, 54.8. (56.) Magnesium bromide, 12; sodium hyposulphite, 72; sodium sulphide, 24; silica and organic matter, 192; hydrogen sulphide, 22.37 c.c. (57.) Copper carbonate, lead and barium sulphates, and arsenic, traces; ammonium chloride, 0.3; strontium sulphate, 29; sodium hyposulphite, 0.5; ammonium nitrate, 0.94; carbon dioxide, 53.7 c.c.; hydrogen sulphide, 10.6 c.c. (58.) Zinc sulphate, 333; ferric sulphate, 2880; aluminium sulphate, 1382; sulphuric acid (free), 97.36; phosphoric acid and ammonia, traces. (59.) Hydrogen sulphide, 70.6 c.c. (60.) Hydrogen sulphide, 1.7 c.c.; a peculiar sulphur compound, 144.

Physiological.—Water is taken into the economy both in its own form and as a constituent of every article of food. Under usual conditions, the amount taken by a healthy adult in twenty-four hours is 2.25 to 2.75 litres, of which 1.75 to 2 litres are taken in the liquid form, the remainder forming a part of the solid food.

The amount of water required by the system is greater when the amount eliminated by the skin and kidneys is increased, as during exposure to high temperature and in diabetes. When the food is dry the amount of water drank is increased.

It constitutes about sixty per cent. of the weight of the body; in all of whose tissues and fluids it exists—most abundantly in the perspiration and saliva (99.5%), and least abundantly in the enamel of the teeth (0.2%). The proportion of water to solids in the body is greater in the earlier years of life:

A fetal mouse contained	880 grams water in 1,000 grams.
A newly born mouse contained	872 grams water in 1,000 grams.
A mouse eight days old contained	768 grams water in 1,000 grams.
A mouse full-grown contained	713 grams water in 1,000 grams.

The consistency of the various parts does not depend entirely upon the relative proportion of solids and water, but is influenced by the nature of the solids. The blood, although liquid in the ordinary sense of the term, contains a less proportional amount of water than does the tissue of the kidneys, and about the same proportion as the tissue of the heart. Although the bile and mucus are not as fluid as the blood, they contain a larger proportion of water to solids than does that liquid.

Water is discharged by the kidneys, intestine, skin, and pulmonary surfaces. The quantity discharged is greater than that ingested; the excess being formed in the body by the oxidation of the hydrogen of its organic constituents.

Hydrogen Dioxide.

Peroxide of Hydrogen—Oxygenated Water—H_2O_2

Discovered by Thénard in 1818. It may be obtained in the pure state by accurately following a tedious process devised by Thénard. In a highly diluted form it is prepared by suspending pure hydrate of barium dioxide in water, through which a rapid current of carbon dioxide is then passed—

$$BaO_2H_2+CO_2=CO_3Ba+H_2O_2,$$

the insoluble barium carbonate being separated by filtration.

Hydrogen dioxide is also formed in small quantities in the slow oxidation of metals, such as lead, zinc, cadmium, nickel, cobalt, and aluminium in damp air, as well as by the slow oxidation of phosphorus, and of many organic substances, essences, alcohol, ether, etc., and in the combustion of coal-gas.

The pure substance is a colorless, syrupy liquid, which, when poured into water, sinks under it before mixing. It has a disagreeable, metallic taste, somewhat resembling that of tartar emetic. When taken into the mouth it produces a tingling sensation, increases the flow of saliva, and bleaches the tissues with which it comes in contact. It has a specific gravity of 1.455, and is still liquid at — 30°. It is very unstable, and, even in darkness and at ordinary temperatures, is gradually decomposed.

At 20° the decomposition takes place more quickly, and at 100° rapidly and with effervescence. The dilute substance, however, is comparatively stable, and may be boiled and even distilled without suffering decomposition.

This substance is subject to singular decompositions, acting both as a reducing and as an oxidizing agent.

It is rapidly decomposed, with evolution of oxygen, by contact with gold or platinum in a state of minute subdivision, powdered charcoal, manganese dioxide, or fibrin—the decomposing agent remaining unaltered.

Many elements and compounds, *e. g.*, arsenic, sulphides, sulphur dioxide, are oxidized when brought in contact with hydrogen peroxide, at the expense of half its oxygen.

If hydrogen peroxide be brought in contact with silver oxide, both are violently decomposed, with evolution of oxygen and liberation of heat and sometimes of light. Water and metallic silver remain.

The pure peroxide, when decomposed, yields 475 times its volume of oxygen; the dilute substance 15 to 20 times its volume.

The presence of peroxide of hydrogen in very minute quantities may be detected by the following tests:

First.—To a solution of starch a few drops of potassium iodide solution are added, then a small quantity of the fluid to be tested, and finally a drop of a solution of ferrous sulphate; if hydrogen peroxide be present, a blue color is observed. This reaction may be obtained with a solution containing only 0.05 milligram per litre (Schoenbein).

Second.—A mixture of tincture of guaiacum and extract of malt strikes a blue color in the presence of oxygenated water. Slightly less delicate than the last (Schoenbein).

Other reactions have been proposed by Schoenbein, Barreswill, Strüve, and Weltzien, which are, however, not characteristic. A colorimetrical method for determining the quantity of hydrogen peroxide has been proposed by Schöne.

Dilute oxygenated water is used for renovating old pictures the whites of which have become dingy by the formation of lead sulphide, which in the renovation is oxidized to the white sulphate.

The various bleaching agents used to convert brunettes into blondes are dilute solutions of oxygenated water.

CLASS II.

ELEMENTS ALL OF WHOSE HYDRATES ARE ACIDS, AND WHICH DO NOT FORM SALTS WITH THE OXACIDS.

I. CHLORINE GROUP.

FLUORINE	F	19
CHLORINE	Cl	35.5
BROMINE	Br	80
IODINE	I	127

The elements of this group are univalent. With hydrogen they form acid compounds, composed of one volume of the element in the gaseous state with one volume of hydrogen. Their hydrates are monobasic acids when they exist (fluorine forms no hydrate). The first two are gases, the third liquid, the fourth solid at ordinary temperatures. Their atomic weights increase from the lowest to the highest by nearly 16 or 16×3. The relations of their compounds to each other are shown in the following table:

HF, Hydrofluoric acid.	——	——	——	——	——	——	——
HCl, Hydrochloric acid.	Cl_2O, Chlorine monoxide.	Cl_2O_3, Chlorine trioxide.	Cl_2O_4, Chlorine tetroxide.	ClOH, Hypochlorous acid.	ClO_2H, Chlorous acid.	ClO_3H, Chloric acid.	ClO_4H, Perchloric acid.
HBr, Hydrobromic acid.	——	——	——	BrOH, Hypobromous acid.	——	BrO_3H, Bromic acid.	BrO_4H, Perbromic acid.
HI, Hydriodic acid.	——	——	I_2O_4, Iodine tetroxide.	IOH, Hypoiodous acid.	IO_2H, Iodous acid.	IO_3H, Iodic acid.	IO_4H, Periodic acid.

FLUORINE.

F or Fl.....19

Although many attempts have been made to isolate this element, it has probably never been obtained in the free state, unless the colorless gas obtained by G. J. and Th. Knox, by the decomposition of mercury fluoride and of hydrofluoric acid in vessels of fluor-spar was the element. The difficulty in the way of its separation lies in the readiness with which it attacks the metals, as well as glass, porcelain, caoutchouc, etc. The source from which the compounds of fluorine are obtained is the natural calcium fluoride, or fluor-spar.

Hydrogen Fluoride.

Hydrofluoric Acid.

HFl.....20

First used for etching on glass, by Schwankhard, in 1670. Scheele, in 1771, discovered the true nature of fluor-spar, and gave this acid the name

of *fluoric acid.* Hydrofluoric acid is obtained by the action of an excess of sulphuric acid upon fluor-spar, with the aid of gentle heat:

$$CaFl_2 + SO_4H_2 = SO_4Ca + 2HFl.$$

If a solution be desired, the operation is conducted in a platinum or lead retort, whose beak is connected with a V-shaped receiver of the same metal, which is cooled and contains a small quantity of water.

The aqueous acid is a colorless liquid, highly acid and corrosive, and having a penetrating odor. In using it great care must be exercised that neither the solution nor the gas come in contact with the skin, as they produce painful ulcers which heal with difficulty, and also constitutional symptoms which may last for days. When the acid has accidentally come in contact with the skin the part should be washed with dilute solution of potash, and the vesicle which forms should be opened.

Its boiling-point is between 15° and 30°. It is still liquid at —40°, and has a specific gravity of 1.06.

The most interesting chemical property of hydrofluoric acid is its action upon glass, from which it removes silica, a reaction which is utilized in the process of etching. For this purpose either the vapor or the solution may be used. In either case the glass surface is coated with a varnish composed of four parts of yellow wax and one part of turpentine, which is then removed from those parts upon which it is desired to act. When the solution is used a wall of wax is built up, and into the reservoir thus formed the liquid is poured; by this method a transparent design is produced. It is more usual to act upon the glass with the vapor, as by this means an opaque and consequently more apparent design is obtained. Some powdered fluor-spar is placed in a shallow leaden dish and moistened with sulphuric acid; the prepared glass plate is then placed, with the waxed surface downward, upon the dish, which is warmed to a temperature not sufficiently elevated to melt the wax.

The presence of fluorine in a compound is detected by reducing the substance to powder, moistening it with sulphuric acid in a platinum crucible, over which is placed a slip of glass prepared as above; at the end of half an hour the wax is removed from the glass, which will be found to be etched if the substance examined contained a fluoride.

Fluorine forms no oxygenated compounds.

CHLORINE.

Cl.....35.5

Although probably first obtained by Glauber, the discovery of this element is usually attributed to Scheele, who discovered it in 1774.

Its true nature was first recognized by Sir Humphrey Davy in 1810. He gave it the name it bears, derived from χλωρός—yellowish green—in reference to its color.

Preparation.—First.—By the process followed by Scheele, the action of manganese dioxide on hydrochloric acid, aided by heat:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The reaction is, however, not as simple as here indicated. Manganic chloride, $MnCl_4$, is first formed and then decomposed into free chlorine and manganous chloride, $MnCl_2$. Only half the chlorine contained in the acid

is liberated, and each kilo of manganese dioxide yields 257.5 litres of chlorine.

Second.—By the action of manganese dioxide upon hydrochloric acid in the presence of sulphuric acid:

$$MnO_2+2HCl+SO_4H_2=SO_4Mn+2H_2O+Cl_2.$$

The same quantity of chlorine is obtained as in *first*, with the use of one-half the quantity of hydrochloric acid.

Third.—By double decomposition of sodium chloride and sulphuric acid, in the presence of manganese dioxide. A mixture of one part each of the two solids, finely powdered, is heated with three parts of sulphuric acid. In this process hydrochloric acid is first formed, according to the equation—

$$SO_4H_2+2NaCl=SO_4Na_2+2HCl.$$

The acid, as soon as found, is decomposed by either of the reactions indicated in *first* and *second*, according as sulphuric acid is or is not present in excess.

Fourth.—By the action of potassium dichromate upon hydrochloric acid:

$$Cr_2O_7K_2+14HCl=2KCl+Cr_2Cl_6+7H_2O+3Cl_2.$$

In this process, which is convenient, although not economical, 2 parts of powdered dichromate are heated with 11 parts of acid of sp. gr. 1.16; the generating flask being immersed in the water-bath. 100 grams of dichromate yield 22½ litres of chlorine.

Fifth.—When a slow evolution of chlorine, extending over a considerable period of time, is desired, as for purposes of disinfection, moistened chloride of lime (see p. 412) is exposed to the air. The calcium hypochlorite is decomposed by the atmospheric carbon dioxide, with liberation of chlorine. If a more rapid evolution of gas be desired, the chloride of lime is moistened with a dilute acid in place of with water.

Chlorine is, at the ordinary temperature and pressure, a greenish yellow gas, has a penetrating odor, and is very irritating to the air-passages, even when highly diluted with air. Its specific gravity is 2.45 A. or 35.5 H. A litre of chlorine at the normal temperature and pressure weighs 3.17 grams. It is quite soluble in water, one volume of which dissolves three volumes of chlorine at 10° C. It must therefor be collected by displacement of air, the disengagement-tube passing to the bottom of the collecting vessel, whose mouth is directed upward.

A saturated solution of chlorine in water is used in the laboratory, where it is known as *chlorine water*; and medicinally under the names *Aqua chlorinii* (*U. S.*), *Liquor chlori* (*Br.*). Good chlorine water bleaches, and does not redden blue litmus.

At a pressure of 6 atmospheres at 0°, or at 8½ atmospheres at 12°, chlorine assumes the form of an oily, yellow liquid, whose density is 1.33, and whose boiling-point is 33.6°. It has not yet been solidified.

Chlorine unites directly with all elements except fluorine, oxygen, nitrogen, and carbon, and with these, fluorine possibly excepted, it is capable of combining indirectly. In many instances the direct union of chlorine with another element is attended by the liberation of light as well as of heat.

At a red heat chlorine decomposes water readily, with the formation of hydrochloric acid and the liberation of oxygen :

$$2H_2O+2Cl_2=4HCl+O_2.$$

The same reaction takes place more slowly at ordinary temperatures, under the influence of sunlight, and for this reason chlorine water must be kept in bottles of yellow glass.

Chlorine is an active bleaching and disinfecting agent in the presence of water. Its action in this respect is that of an indirect oxydant; it decomposes water, liberating oxygen, which then attacks the coloring or odorous organic matter.

In many instances chlorine acts directly upon organic matters, a portion uniting with an equivalent number of atoms of hydrogen to form hydrochloric acid ; while another portion takes the place of the atoms of hydrogen thus displaced. Thus, with marsh-gas, hydrochloric acid and methyl chloride are formed :

$$CH_4+Cl_2=CH\,Cl+HCl.$$

Chlorine is capable of forming a definite hydrate, having the composition $Cl.5H_2O$, which is a yellowish green, crystalline substance, formed when chlorine is passed through chlorine water cooled to 2°—3°, and is again decomposed when the temperature reaches 10°.

Compounds of Chlorine.

Hydrogen Chloride.

Hydrochloric acid—Muriatic acid—Acidum muriaticum (*U. S.*)—*Acidium hydrochloricum* (*Br.*).—HCl.—Although known to the alchemists, in solution, as *spirits of salt*, hydrochloric acid exists in nature in small quantities only; in volcanic gases and in the gastric juice of the mammalia (p. 75).

The source whence hydrochloric acid is obtained, either as an incidental product or by a special process, is sodium chloride.

One of the steps of Leblanc's process for the manufacture of sodium carbonate is the decomposition of sodium chloride by sulphuric acid:

$$2NaCl+SO_4H_2=SO_4Na_2+2HCl.$$

The acid, thus liberated, being very deleterious to both vegetable and animal life, is passed through suitably arranged towers, where it meets a descending stream of water, in which it is dissolved to form, after concentration, the muriatic acid of commerce. As Leblanc's process is being gradually superseded by another in which hydrochloric acid is not liberated (see p. 398), the acid is now specially prepared by the same reaction.

Hydrochloric acid is formed in a number of other reactions, none of which, however, has been utilized for its industrial production. One which is of theoretical interest, is by the direct union of its constituents: one volume of hydrogen and one of chlorine unite, under the influence of sunlight, to form two volumes of hydrochloric acid gas.

Hydrochloric acid is a colorless gas, having an acid reaction, an acid taste, a sharp, penetrating odor, and producing great irritation of any tissue with which it comes in contact. Its specific gravity is 1.264 A or 36.5 H. A litre weighs, at 0° and 760 mm., 1.6352 grams. When subjected to a pressure of 40 atmospheres at 4°, gaseous hydrochloric acid assumes the liquid form. In contact with moist air it forms white clouds. It does not burn in air, nor does it support combustion. It is very soluble in water; one volume of water at 0° dissolving 480 volumes, and at the ordinary temperature 460 volumes.

The muriatic or hydrochloric acids used in the arts and in pharmacy are solutions of the gas in water of different degrees of purity and concentration. A pure, saturated solution in pure water is a clear, colorless liquid, has a strongly acid taste and reaction, a specific gravity of 1.2, and gives off white fumes when exposed to the air. Non-saturated solutions have lower specific gravities, according to the degree of concentration.

SPECIFIC GRAVITIES OF SOLUTIONS OF HYDROCHLORIC ACID (*Ure*).

Specific gravity.	Acid of sp. gr. 1.2 in 100 pts.	HCl in 100 pts.	Specific gravity.	Acid of sp. gr. 1.2 in 100 pts.	HCl in 100 pts.	Specific gravity.	Acid of sp. gr. 1.2 in 100 pts.	HCl in 100 pts.
1.2000	100	40.777	1.1349	67	27.321	1.0657	33	13.094
1.1982	99	40.369	1.1328	66	26.913	1.0637	32	12.597
1.1964	98	39.961	1.1308	65	26.508	1.0617	31	12.300
1.1946	97	39.554	1.1287	64	26.098	1.0597	30	11.903
1.1928	96	39.146	1.1267	63	25.690	1.0577	29	11.506
1.1910	95	38.738	1.1247	62	25.282	1.0557	28	11.109
1.1893	94	38.330	1.1226	61	24.874	1.0537	27	10.712
1.1875	93	37.923	1.1206	60	24.466	1.0517	26	10.316
1.1857	92	37.516	1.1185	59	24.058	1.0497	25	9.919
1.1846	91	37.108	1.1164	58	23.650	1.0477	24	9.522
1.1822	90	36.700	1.1143	57	23.242	1.0457	23	9.126
1.1802	89	36.292	1.1123	56	22.834	1.0437	22	8.729
1.1782	88	35.884	1.1102	55	22.426	1.0417	21	8.332
1.1762	87	35.476	1.1082	54	22 019	1.0397	20	7.935
1.1741	86	35.068	1.1061	53	21.611	1.0377	19	7.538
1.1721	85	34.660	1.1041	52	21.203	1.0357	18	7.141
1.1701	84	34.252	1.1020	51	20.796	1.0337	17	6.745
1.1681	83	33.845	1.1000	50	20.388	1.0318	16	6.348
1.1661	82	33.437	1.0980	49	19.980	1.0308	15	5.951
1.1641	81	33.029	1.0960	48	19.572	1.0279	14	5.554
1.1620	80	32.621	1.0939	47	19.165	1.0259	13	5.158
1.1599	79	32.213	1.0919	46	18.757	1.0239	12	4.762
1.1578	78	31.805	1.0899	45	18.340	1.0220	11	4.365
1.1557	77	31.398	1.0879	44	17.941	1.0200	10	3.998
1.1536	76	30.990	1.0859	43	17.534	1.0180	9	3.571
1.1515	75	30.582	1.0838	42	17.126	1.0160	8	3.174
1.1494	74	30.174	1.0818	41	16.718	1.0140	7	2.778
1.1473	73	29.767	1.0798	40	16.310	1.0120	6	2.381
1.1452	72	29.359	1.0778	39	15.902	1.0110	5	1.984
1.1431	71	28.951	1.0758	38	15.494	1.0080	4	1.588
1.1410	70	28.544	1.0738	37	15.087	1.0060	3	1.191
1.1389	69	28.136	1.0718	36	14.679	1.0040	2	0.795
1.1369	68	27.728	1.0697	35	14.271	1.0020	1	0.397
			1.0677	34	13.863			

The boiling-point of hydrochloric acid solution varies with the concentration. It is the highest, 111.11°, with an acid of sp. gr. 1.094. When concentrated hydrochloric acid is boiled, the totality of the gas is not expelled; when it reaches the composition of the hydrate HCl, $8H_2O$, nearly corresponding to the specific gravity given above, its boiling-point remains stationary and an acid of the same composition distils over.

The varieties of the acid solutions used in the arts and in medicine are :

Commercial muriatic acid, a yellow liquid; specific gravity about 1.16; contaminated with iron, with chloride of sodium, and with arsenical compounds. It is used only for manufacturing and coarse chemical processes.

C. P. hydrochloric acid, a colorless liquid, usually far from pure (see below).

Acidum muriaticum (*U. S.*)—*Acidum hydrochloricum.* (*Br.*), a colorless liquid, of sp. gr. 1.16=32.3% of the gaseous acid, which contains small quantities of impurities.

Acidum muriaticum dilutum (*U. S.*)—*Acidum hydrochloricum dil.* (*Br.*).—The last, diluted with water to sp. gr. 1.038, U. S. (1.052, Br.), and containing 7.74 per cent. HCl. (10.6 per cent., Br.).

Hydrochloric acid is ranked, with nitric and sulphuric acids, as one of the strong mineral acids. It is decomposed by many metals, with liberation of hydrogen and formation of a chloride:

$$2HCl+Zn=ZnCl_2+H_2.$$

With oxides and hydrates it enters into double decomposition, forming water and a chloride:

$$CaO+2HCl=CaCl_2+H_2O.$$

$$CaH_2O_2+2HCl=CaCl_2+2H_2O.$$

Most of the metallic chlorides are readily soluble in water, mercurous, silver, and lead chlorides being exceptions.

By the action of oxidizing agents, hydrochloric acid is decomposed with liberation of chlorine, as in the reaction between it and potassium dichromate (p. 71). The chlorine, being thus in the nascent state, is capable of uniting with gold or platinum to form chlorides of those metals. The same liberation of chlorine takes place in the mixture of nitric and hydrochloric acids, in the proportion of one molecule of the former to three of the latter, known as *Aqua regia*, *Acid. nitro-muriaticum* (*U. S.*), *Acid. nitro-hydrochloricum* (*Br.*).

Compounds formed by the substitution of a metal or radical for the hydrogen of hydrochloric acid are called *chlorides.*

Analytical.—The presence of hydrochloric acid, or of a chloride in solution, may be detected by the formation of a white, flocculent precipitate with silver nitrate, which is soluble in ammonia, but insoluble in nitric acid (see p. 81).

Impurities.—Hydrochloric acid should be perfectly colorless. It should give no coloration with potassium sulphocyanate (iron). When shaken with chloroform, the latter should not be colored (bromine and iodine). It should not precipitate with solution of barium chloride, in

solution of sulphur dioxide (chlorine). It should give no reaction when tested for arsenic by Otto's method.*

Physiological.—The existence of free hydrochloric acid in the gastric juice was first noted by Prout in 1824, and proved by Schmidt in 1852. Although Lehmann, Blondlot, Bernard and others have thought otherwise, subsequent investigations have fully confirmed the results of Schmidt.

Toxicology.—Notwithstanding the frequent use of this acid in the arts, it is very rarely administered with murderous intent, owing to its pronounced odor and taste. Several cases are recorded, however, in which it has been taken either by accident, or with suicidal intent. Its action is similar to that of sulphuric acid (*q. v.*), but not as intense, except in so far as the larynx is concerned. The treatment consists in neutralizing the acid as quickly as possible by the administration of an alkali, or of magnesia.

The detection of the acid in the body after death requires a quantitative determination. Stains produced by the acid upon colored cloth are of a brighter red than those produced by sulphuric acid, and do not destroy the fibre of the cloth to so great an extent. They disappear when moistened with aqua ammoniæ, if they be not too old.

Distinction between poisons and corrosives.—Although the deleterious action exerted by certain substances when they are taken into the stomach in small quantities has been known and made use of by the evilly inclined from the earliest antiquity, the definition of a poison has been difficult. The element of quantity, although it is an important factor in the method of action of deleterious substances, does not afford ground upon which to base the desired definition, as it is impossible to fix definitely the dose of any poison which is necessarily lethal. Almost all substances, if taken in sufficient quantity, produce derangements which may terminate in death.

There is this distinction between the methods of action of true poisons and of corrosives, such as the mineral acids: the former do not reveal their lethal character *until they have been absorbed into the circulation;* the latter act, not through the blood, but by coming into immediate contact with and destroying some organ essential to life. Sulphuric acid will destroy life as surely by disintegrating a large surface of skin as it will by corroding the coats of the stomach. Both actions are due to the same quality of the acid, yet, if we include sulphuric acid among the poisons, we are forced to the unphilosophical conclusion of considering it a poison when it destroys the stomach, but not when it corrodes another equally essential organ.

The best definition of a poison we believe to be the following: *Any substance which, after absorption into the blood, produces death or serious bodily harm.* The question of quantity is thus avoided, and, according to our definition, as in accordance with fact, the same substance is or is not a poison, as it is taken in quantities sufficient or insufficient to produce harmful results.

The mineral acids and alkalies, acting at their points of immediate contact with the tissues, find a place medically and toxicologically under the head of *corrosives*, and legally among the "other noxious or destructive things" mentioned in statutes relating to poisoning.

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* Ausmittel d. Gifte, 5th ed., p. 97, note.

Compounds of Chlorine and Oxygen.

Three compounds of chlorine and oxygen have been isolated, two being anhydrides. They are all very unstable, and prone to sudden and violent decomposition.

Chlorine monoxide, Cl_2O=*hypochlorous anhydride* or *oxide*, is obtained by the action of dry chlorine upon cooled, precipitated mercuric oxide—

$$HgO+2Cl_2=HgCl_2+Cl_2O,$$

as a blood-red, mobile liquid below 20°. Above that temperature it is a reddish yellow gas, having a penetrating odor similar to that of chlorine. It is decomposed with an explosion upon the slightest jar, and even spontaneously. When brought into contact with water it slowly forms a nearly colorless solution, containing *hypochlorous acid*, ClOH, which may be more readily obtained in solution by passing a current of chlorine through water holding recently precipitated calcium carbonate in suspension, and subjecting the solution to distillation, the receiver being well cooled.

This solution is a yellow liquid, having an acrid taste and an odor of chlorine. It is an exceedingly active oxidizing and bleaching agent. Owing to its instability, the acid itself is not used industrially, although its salts, the hypochlorites of calcium, potassium and sodium are (see pp. 412, 401, 398).

Chlorine trioxide, Cl_2O_3=*chlorous anhydride* or *oxide*, is obtained by the action of dilute nitric acid upon potassium chlorate, in the presence of arsenic trioxide. It is a greenish yellow gas; decomposes at about 50° C., with explosion; soluble in water; has strong bleaching powers, and an irritating action upon the air-passages when inhaled. Its aqueous solution contains *chlorous acid*, ClO_2H—a very unstable body, which has not been isolated, corresponding to a series of salts called *chlorites*.

Chlorine tetroxide, Cl_2O_4=*chlorine peroxide*, a violently explosive body, obtained by the action of concentrated sulphuric acid upon potassium chlorate. Below —20° it is an orange-red liquid, and above that temperature a yellow gas, probably composed of Cl_2O+Cl_2O. Although this body is sometimes improperly called *hypochloric acid*, there is no corresponding hydrate; and if it be brought in contact with an alkaline hydrate, a mixture of the chlorate and chlorite of the metal is formed:

$$Cl_2O_4+2KHO=ClO_3K+ClO_2K+H_2O.$$

Besides the above, there exist two other oxacids of chlorine, whose corresponding anhydrides have not been isolated. These are chloric and perchloric acids.

Chloric acid, ClO_3H—obtained in aqueous solution, by decomposing its barium salt with the proper quantity of dilute sulphuric acid. As thus obtained, it is a syrupy liquid, colorless or yellowish, and strongly acid. It decomposes at 40°, and is an energetic oxydant.

Perchloric acid, ClO_4H—the most stable of the series, is prepared by boiling potassium chlorate with hydrofluosilicic acid, cooling, decanting the clear fluid, which is evaporated and from time to time decanted until

white fumes appear, when it is distilled. It is a colorless, oily liquid, sp. gr. 1.782; explodes on contact with organic substances or charcoal; corrodes animal tissues energetically.

It enters into the composition of *chlorodyne.*

BROMINE.

Br.....80

Discovered by Balard in 1826. Its name is derived from βρῶμος, an evil odor. It does not exist free in nature, but is found in combination with the alkaline metals and magnesium, widely diffused, but in small quantities.

It is obtained from the mother-liquors of salt springs, especially those of Stassfurth and Kreuznach in Germany, and of Pomeroy, Ohio; from the mother-liquor left in the manufacture of sea-salt; and from kelp (see p. 78). These are subjected to distillation with manganese dioxide and sulphuric acid, by which the bromides are decomposed and elementary bromine liberated.

At ordinary temperatures, bromine is a dark, reddish brown liquid; has a strong, disagreeable odor, somewhat resembling that of chlorine; is irritating to the air-passages, and corrodes animal tissues with which it comes in contact.

It is volatile at all temperatures above its point of solidification, giving off red fumes. It boils at 63°. Its freezing-point is variously given from — 7.3° to — 24.5°. The latter is probably the correct one, the higher freezing-points of some samples being due to the presence of water. Sp. gr. 3.1872 at 0°. Soluble in water to the extent of 3.2 parts in 100 at 15°. When the solution is cooled to 0° in the presence of an excess of bromine, a crystalline hydrate, $Br.5H_2O$, is formed. It is more soluble in alcohol, carbon disulphide, chloroform, and ether, than in water. Its solutions, which are yellow or brown, according to concentration, are decomposed by exposure to light, with formation of hydrobromic acid.

Its chemical properties are the same as those of chlorine in kind, but less energetic.

It is highly poisonous, but, owing to its comparative rarity and its powerful odor, only one case of death from its action has been recorded.

Free bromine may be recognized by its odor, by the yellow or brown color of its chloroform solution, and by the yellow or orange color which it communicates to starch paste. (For the analytical reactions of the bromides, see p. 81.)

Hydrogen Bromide.

Hydrobromic acid, HBr.—This acid cannot be obtained by decomposition of a bromide as hydrochloric acid is obtained by decomposition of a chloride, as it is destroyed by the presence of any excess of sulphuric acid. It is obtained by the action of water upon phosphorus tribromide—

$$PBr_3+3H_2O=PO_3H_3+3HBr,$$

or by the action of bromine upon paraffine.

It is a colorless gas; produces white clouds on contact with air; liquefies at —69°, and solidifies at —73°; has an acid taste and reaction, and

dissolves readily in water, with which it forms a definite hydrate, HBr $2H_2O$. Its chemical properties are similar to those of the corresponding chlorine compound. Its hydrogen is replaceable by metals to form bromides.

Oxacids of Bromine.

No oxides of bromine are known, although three oxacids exist, either in the free state or as salts:

Hypobromous acid—BrOH—may be obtained, in aqueous solution, by the action of bromine upon mercuric oxide, silver oxide, or silver nitrate. When bromine is added to concentrated solution of potassium hydrate, no hypobromite is found, but a mixture of bromate and bromide, having no decolorizing action. With sodium hydrate, however, sodium hypobromite is formed in solution, and such a solution, freshly prepared, is used in Knop's process for determining urea (p. 264).

Bromic acid—BrO_3H—is readily obtained, in aqueous solution, by the action of chlorine upon bromine, in the presence of water, or by the decomposition of barium bromate, suspended in water, by sulphuric acid. In combination as a bromate, it is obtained by the action of bromine upon a solution of potassium hydrate—

$$6KHO+3Br_2=BrO_3K+5KBr+3H_2O,$$

the bromate being separated from the bromide by taking advantage of its more sparing solubility.

Perbromic acid—BrO_4H—is obtained as a comparatively stable, oily liquid, by the decomposition of perchloric acid by bromine, and concentrating over the water-bath. It is noticeable in this connection that, while hydrochloric acid and the chlorides are more stable than the corresponding bromine compounds, the oxygen compounds of bromine are more permanent than those of chlorine.

IODINE.

I.....127

Discovered in 1811 by Courtois; further studied by Gay-Lussac in 1814, and by Sir H. Davy at about the same time. Name derived from ἰώδης, violet, referring to the color of its vapor.

Iodine has not been found to exist in nature in the free state, but in combination it is widely disseminated in the three kingdoms of nature, without, however, being anywhere abundant. The iodides of potassium, sodium, calcium, and magnesium exist in small quantities in sea-water, in the waters of mineral springs, and indeed, in mere traces, in most natural waters; more abundantly in the ashes of marine plants, sponges, molluscs and polyps, as well as in the bodies of animals living in salt water. Cod-liver oil contains appreciable quantities of iodine—according to De Jongh, 37 parts in 100,000.

Iodine is obtained almost exclusively from the ashes of sea-weeds collected in Scotland and in the north of France. The weeds are burned, and the ash, known as *kelp* in Scotland, and as *varech* in France, is extracted with water, and the solution subjected to fractional crystalliza-

tion. The last concentrated mother-liquid, which refuses to crystallize, contains the iodides; they are decomposed by a current of chlorine, aided by heat; the iodine being thus driven off, is collected in suitable condensing-chambers.

It occurs in iron-gray, brittle, crystalline scales, having a metallic lustre, and a sp. gr. of 4.948 at 17°. It melts at 113.6° and boils at 175°. Its vapor is of a rich violet color. It volatilizes at all temperatures, the vapor condensing in the crystalline form. The density of the vapor is 8.716 A, or 127 H. It has a peculiar and characteristic odor, and a disagreeable taste; is sparingly soluble in water, which takes up a larger quantity, however, on standing over an excess of iodine—owing to the formation of hydriodic acid, in a solution of which iodine is more soluble than in pure water. The solubility of iodine is very much increased by the presence of certain salts, notably of potassium iodide. A solution of iodine in solution of potassium iodide is used in medicine, under the names *Liq. iodinii compositus* (*U. S.*), *Liq. iodi* (*Br.*), *Lugol's solution.* Iodine is soluble in alcohol (*Tinct. iodinii*), and in ether with a brown color; in chloroform, benzol, and carbon disulphide, with a violet color.

Its chemical properties are similar to those of chlorine and bromine, but less marked. In the presence of water, iodine exerts a slight oxidizing and decolorizing action. It decomposes hydrogen sulphide with liberation of elementary sulphur and formation of hydrogen iodide. It does not combine with ordinary oxygen, but does with ozone. It unites directly with many of the metalloids, and with most of the metals, to form iodides. It dissolves in solution of potassium hydrate, with formation of potassium iodide and some hypoiodide. Nitric acid oxidizes it to iodic acid. With ammonium hydrate it forms nitrogen iodide (*q. v.*).

Free iodine may be detected by the blue-violet color which it communicates to starch, and by the violet color of its solutions in carbon disulphide and chloroform.

Commercial iodine is liable to contamination with foreign substances. Of these, non-volatile bodies, such as manganese dioxide, graphite, etc., may be detected and separated by subliming the iodine. Water has been found to be used as an adulterant of iodine in as large quantity as twenty per cent.; it renders the iodine moist and sticky; and when iodine so adulterated is dissolved in carbon disulphide, the water separates in a distinct layer. Chlorides of calcium and magnesium have also been detected in iodine. The most serious contamination, however, is that with the iodide of cyanogen, which is probably formed during the process of manufacture, by the decomposition of cyanides contained in the kelp. The scales of iodine so contaminated have upon their surfaces minute, white, acicular crystals. To detect and at the same time separate this impurity when present even in very small quantities, heat one ounce of the iodine over the water-bath in a porcelain dish, covered by a flat-bottomed flask containing cold water. After about twenty minutes' heating the iodide of cyanogen will have collected on the bottom of the flask, in white acicular crystals.

Action on the Economy.

When brought in contact with the skin it produces irritation and a brown stain, which, however, soon disappears. When taken internally, it acts both as a local irritant to the surfaces of the intestinal canal, with which it comes in contact, and as a true poison. Cases of acute iodine

poisoning are not common, and those recorded are due to accident or negligence, with one exception, in which homicide was prevented by the color communicated to the starchy fluid with which the iodine was mixed. It is probable that when iodine is administered internally, it is converted into hydriodic acid (*q. v.*) during the processes of assimilation. At all events, it is ultimately discharged as an alkaline iodide by the urine and saliva, but not by the perspiration, whether it be taken as free iodine or as potassium iodide; when taken in large quantities, it also appears in the fæces. The treatment consists in removing the poison by emetics or the stomach-pump, as rapidly as possible.

Hydrogen Iodide.

Hydriodic acid—HI.—Hydriodic acid does not exist in nature. For its preparation recourse is had to the decomposition of phosphorus triiodide by water:

$$PI_3+3H_2O=PO_3H_3+3HI.$$

Red phosphorus is placed in a retort, under water; the proper quantity of iodine is then added and the retort heated.

When desired in solution, it is more readily obtained by directing a current of hydrogen sulphide through water holding iodine in suspension—

$$H_2S+I_2=2HI+S,$$

and filtering from the precipitated sulphur. This is the method directed by the U. S. P.

Hydrogen iodide is a colorless gas, fuming on contact with air, having a strong acid reaction and a penetrating odor. Sp. gr. 4.443 A—64.2 H. By cold and pressure it may be condensed to a yellow liquid, which solidifies at −55°. It is very soluble in water, one volume of which, at 10°, dissolves 425 volumes of the gas. The saturated solution has a density of 1.7. When heated, like hydrochloric acid solution, it gives off a part of its gas, until the boiling-point becomes stationary at 126°, when the remainder distils without decomposition.

Hydriodic acid is decomposed into its component elements when heated—the decomposition being only partial, as the same influence brings about a partial union of the elements. When a mixture of hydriodic acid and oxygen is ignited, iodine is set free and water is formed. The same action takes place when the mixture is exposed to sunlight. Aqueous solutions of hydriodic acid, when exposed to the light, quickly become brown from a decomposition of the acid, with separation of elementary iodine. Hydriodic acid is also decomposed by a number of other substances; by many metals with formation of metallic iodides and liberation of hydrogen; by chlorine and bromine with liberation of iodine; by sulphuric and nitric acids, also with liberation of iodine; and by many chlorides, with formation of hydrochloric acid and an iodide:

$$PCl_3+3HI=PI_3+3HCl.$$

The readiness with which it gives up its hydrogen renders it a valuable source of that element in the nascent state, for which purpose it is used in organic chemistry.

In aqueous solution it is officinal in the U. S. P. as *Acid. hydriodicum dil.*, which, however, is very prone to decomposition.

Analytical Characters.

Chlorides, bromides, and iodides.—The detection and determination of any one of these classes of compounds is simple in the absence of the other two. When it is uncertain, as is usually the case, whether there be not two or more of them present, the determination becomes more difficult. Silver nitrate forms a precipitate with either of the three, which is white, or yellowish if the bromide or iodide be present in large quantity, and is insoluble in dilute nitric acid. Ammonium hydrate dissolves the precipitate very readily in the case of the chloride, much less readily in that of the bromide, and with great difficulty in that of the iodide.

The best means of distinguishing between the three is by adding a few drops of carbon disulphide and chlorine water; upon shaking the mixture the disulphide is colored violet in the presence of an iodide, yellow or orange by bromine, and remains colorless if neither bromide nor iodide be present.

Cyanides also give a white precipitate with silver nitrate, insoluble in dilute nitric acid and rather soluble in ammonium hydrate; they are detected by the characters given on p. 340.

For the methods of detecting small quantities of these salts in the presence of each other, and for their estimation, see the works of Rose, Fresenius, and Gerhard and Chancel.

Oxacids of Iodine.

The best known of these are the highest two of the series—iodic and periodic acids.

Iodic acid—IO_3H—does not exist in nature. It is formed as an iodate, whenever iodine is dissolved in a solution of an alkaline hydrate—

$$I_6+6KHO=IO_3K+5KI+3H_2O,$$

as the free acid, by the action of strong oxidizing agents, such as nitric acid or chloric acid, upon iodine; or by passing chlorine for some time through water holding iodine in suspension. The preparation and purification of iodic acid are always tedious.

Iodic acid appears in white crystals, decomposable at 170°, and quite soluble in water, the solution having an acid reaction, and a bitter, astringent taste.

It is an energetic oxidizing agent, yielding up its oxygen readily, with separation of elementary iodine or of hydriodic acid. It is used as a test for the presence of morphine (*q. v.*).

Periodic acid; IO_4H—is formed by the action of chlorine upon an alkaline solution of sodium iodate. The sodium salt thus obtained is dissolved in nitric acid, treated with silver nitrate, and the resulting silver periodate decomposed with water. From the solution the acid is obtained in colorless crystals, fusible at 130°, very soluble in water, and readily decomposable by heat.

II. SULPHUR GROUP.

SULPHUR	S	32
SELENIUM	Se	79.5
TELLURIUM	Te	128

The elements of this group are divalent. With hydrogen they form compounds composed of one volume of the element, in the form of vapor, with two volumes of hydrogen—the combination being attended with a condensation in volume of one-third. Their hydrates are dibasic acids. They are all solid at ordinary temperatures. The relation of their compounds to each other are shown in the following table:

H_2S, Hydrogen sulphide.	SO_2, Sulphur dioxide.	SO_3, Sulphur trioxide.	SO_2H_2, Hyposulphurous acid.	SO_3H_2, Sulphurous acid.	SO_4H_2, Sulphuric acid.
H_2Se, Hydrogen selenide.	SeO_2, Selenium dioxide.	SeO_3, Selenium trioxide.	——	SeO_3H_2, Selenious acid.	SeO_4H_2, Selenic acid.
H_2Te, Hydrogen telluride.	TeO_2, Tellurium dioxide.	TeO_3, Tellurium trioxide.	——	TeO_3H_2, Tellurous acid.	TeO_4H_2, Telluric acid.

SULPHUR.

S.....32

This element has been known in its own form from remote antiquity. It was called *θεῖον* by the Greeks. It occurs in actively volcanic regions, in crystalline powder, in large crystals, or amorphous. It is brought principally from Sicily, Iceland, and the vicinity of Naples, where it is found near "solfataræ," which are vents in the craters of extinct volcanoes, through which gases still issue.

The native sulphur is always accompanied by more or less earthy matter, from which it is separated by two distillations: one in the locality where it is collected, the product of which is *crude sulphur;* and a second, in a more perfect apparatus, which yields *refined sulphur.* This is in one of two forms. During the first portion of the distillation, while the air of the condensing-chamber is still cool, the vapor of sulphur is condensed in the form of a fine powder, known as *flowers of sulphur,* and composed of minute crystals. At a later stage, when the temperature of the condensing-chamber reaches 114°, the sulphur collects at the bottom as a liquid; this is drawn off from time to time, and cast into elongated, conical moulds, forming *roll sulphur.* Its physical properties are affected by various conditions. Generally, sulphur appears as a light yellow solid, having neither taste nor odor. At low temperatures (below −50°), and when in a state of fine subdivision, it is almost colorless.

It is dimorphous; crystallizes in oblique rhombic prisms when fused sulphur is allowed to solidify, and in rhombic octohedra when its solution

in carbon disulphide is allowed to evaporate spontaneously. The two forms differ from each other in specific gravity: that of the prismatic sulphur being 1.95, and that of the octohedral 2.05. The fusing-point of the first variety is 120°; that of the second 114.5°. The prismatic variety does not remain such indefinitely; transparent at first, it gradually becomes opaque from a conversion of the prisms into collections of octohedra.

When sulphur is heated it melts to a thin, yellow liquid at about 114°; at from 150° to 160° this becomes thick and brown; toward 330° to 340° it becomes thinner and lighter in color again, and, finally, it boils at a temperature variously stated from 440° (Deville) to 448° (Becquerel), giving off a brownish yellow vapor. When heated to about 400° and suddenly cooled, it is converted into still another variety, known as *plastic sulphur*, which, for a time, is reddish brown, transparent, elastic, and so soft that it may be moulded into any desired form. At 1,000° the density of vapor of sulphur is 2.22A or 31.75H. The best solvents of sulphur are protochloride of sulphur and carbon disulphide, a solution in the former containing 66.7 per cent. of sulphur at ordinary temperatures, and the latter dissolving 37.2 parts per 100 at 15°. It is also soluble to a less extent in aniline, phenol, benzol, benzine, and chloroform.

Sulphur may be obtained as a white, very finely divided powder, by the decomposition of calcium sulphide. As thus prepared, it is the *Sulphur præcipitatum* (U. S., Br.), or *milk of sulphur*.

Sulphur unites readily with other elements, forming compounds which, except those formed with elements of the chlorine group and oxygen, are known as sulphides. When heated in contact with air or oxygen, it burns with a blue flame, giving off sulphur dioxide, SO_2. In an atmosphere of hydrogen it burns with formation of hydrogen sulphide.

The compounds of sulphur resemble in composition, and to some extent in their chemical properties, the corresponding oxygen compounds when these exist. Thus, carbon disulphide, CS_2, is an anhydride corresponding to carbon dioxide, CO_2. In many organic substances sulphur may be made to replace oxygen; thus, we have sulphocyanic acid, CNSH, corresponding to cyanic acid, CNOH. Sulphur is used in the arts, principally for the manufacture of gunpowder; also to some extent in making sulphuric acid, sulphur dioxide, and matches, and for the prevention of parasitic growths. It is not used medicinally to the same extent as formerly. We have only theoretical explanations of the method in which it is rendered capable of absorption. That it is absorbed when taken internally is, however, certain, from the fact that persons taking it excrete by the skin sufficient quantities of some compound of sulphur to blacken silver coins carried in their clothing.

Compounds of Hydrogen and Sulphur.

Two of these are known—similar in composition to the oxygen compounds:

Hydrogen sulphide.....H_2S.
Hydrogen persulphide.....H_2S_2.

It is probable that there also exist other compounds containing a still higher proportion of sulphur.

Hydrogen Sulphide.

Sulphydric acid—Hydrosulphuric acid—Sulphuretted hydrogen—H_2S—exists in nature in the volcanic gases; as a result of the decomposition of organic matters containing sulphur; and in solution in the waters of some mineral springs.

It may be obtained by the direct union of the elements, either by burning sulphur in hydrogen, or by passing a current of hydrogen through molten sulphur. At high temperatures vapor of sulphur decomposes water with formation of hydrogen sulphide and pentathionic acid. It is also formed by the action of nascent hydrogen upon sulphuric acid, in the presence of zinc, if the mixture become heated. This last method of formation is of interest in connection with Marsh's test for arsenic (*q. v.*).

When desired in the laboratory, it is obtained by one of the three following reactions:

First.—By the action of hydrochloric acid upon antimony trisulphide:

$$Sb_2S_3+6HCl=2SbCl_3+3H_2S.$$

Second.—The process usually adopted is by the action of diluted sulphuric acid upon ferrous sulphide:

$$FeS+SO_4H_2=SO_4Fe+H_2S.$$

Third.—When the gas is required for toxicological analysis, it is essential that it should contain no hydrogen arsenide (which has been shown by Myers to be capable of existence in the presence of hydrogen sulphide); and as it is difficult to obtain ferrous sulphide free from arsenic, which would be converted into hydrogen arsenide under the conditions required for the formation of hydrogen sulphide, Otto has recommended that hydrogen sulphide be obtained in such cases by the action of hydrochloric acid upon calcium sulphide (*q. v.*):

$$CaS+2HCl=CaCl_2+H_2S.$$

By whatever method hydrogen sulphide is prepared, it must be washed before use by bubbling through water.

Hydrogen sulphide is a colorless gas, having the odor of rotten eggs, and a correspondingly disgusting taste; sp. gr. 1.19 A—17.2 H. Water at 15° dissolves 3.23 times its volume of the gas, which is also soluble in alcohol. At −74°, at the ordinary pressure, or under a pressure of 17 atmospheres, it liquefies; and solidfies at −85.5°, into white crystals. The density of the liquid is 0.9.

Hydrogen sulphide burns in air with formation of sulphur dioxide and water:

$$2H_2S+3O_2=2SO_2+2H_2O.$$

If the supply of oxygen be deficient, water is formed and elementary sulphur deposited:

$$H_2S+O=H_2O+S.$$

Mixtures of hydrogen sulphide and oxygen, or air, explode on the approach of a flame. When hydrogen sulphide in solution is exposed to

the air, it is decomposed into separation of sulphur. Solutions should be made with boiled water and kept in bottles, which are completely filled and well corked. Oxidizing agents decompose hydrogen sulphide readily with separation of sulphur; it is also similarly decomposed by chlorine, bromine and iodine, which unite with its hydrogen. Sulphur dioxide and hydrogen sulphide mutually decompose each other (see p. 87).

When the gas is passed through a solution of an alkaline hydrate, the oxygen of the hydrate is displaced by sulphur, with formation of a sulphydrate:

$$H_2S+KHO=H_2O+KHS.$$

When directed through a solution of a metallic salt, hydrogen sulphide relinquishes its sulphur to the metal—

$$SO_4Cu+H_2S=CuS+SO_4H_2$$

—a property which renders it of great value in analytical chemistry.

The presence of hydrogen sulphide, even in minute quantities, may be detected by its odor, and by the brown or black coloration which it produces in a piece of filter-paper moistened with solution of lead acetate.

Action on the Economy.

Hydrogen sulphide exists in small quantity in the gases of the intestine, where it results from the decomposition of albuminous material, or from that of taurocholic acid; it also occurs occasionally in abscesses and in the urine in tuberculosis, variola, and cancer of the bladder, resulting from the decomposition of some unknown sulphurized body. In certain exceptional cases the gas may also reach the bladder by diffusion from the rectum (Betz).

When inhaled, hydrogen sulphide is an active poison. An animal placed in an atmosphere of the gas dies almost immediately, and the moderately diluted gas is still rapidly fatal. The minimum proportion in which it is fatal to human life is stated by Letheby to be one per cent., although Gaultier de Claubry claims that workmen have existed for some time in an atmosphere containing three per cent. Even when highly diluted, it produces, when inhaled, a low, febrile condition; and care should be had that the air of laboratories in which it is used is not contaminated by it.

The researches of Kaufmann and Rosenthal, Diakonaw and Preyer, leave no doubt that the toxic effects of hydrogen sulphide are due primarily, if not entirely, to its reducing and combining with the coloring-matter of the red blood-corpuscles.

Sewer-gases.—It is but rarely that a human being inhales simple mixtures of air with hydrogen sulphide. The latter generally produces its deleterious effects as a constituent of the gases emanating from sewers, privies, burial-vaults, etc., in which it exists both in its own form and as ammonium sulphydrate. Cases of accidental (if the adjective be admissible) poisoning from sewer-gases are of two forms: 1. Slow poisoning, sometimes terminating fatally, by sewer-gases diluted with air and traceable to defective plumbing; generally in dwellings "fitted with all the modern conveniences." Very common, although easily preventable by

proper trapping and ventilation of soil- and waste-pipes. 2. Cases which may be designated as acute, in which the gas is inhaled in a more concentrated form, as by those entering sewers or engaged in the removal of night-soil. The victim usually falls as if by the effect of a sudden blow, and, even if rescued within a few moments, frequently dies within twenty-four hours.

The treatment should consist in promoting the inhalation of fresh air—by artificial respiration if necessary, cold affusions, the administration of hot brandy and water, and the inhalation of air containing a trace of chlorine.

In cases of death the blood is very dark in color, and on spectroscopic examination shows the bands of sulphæmoglobin.

Sulphur Dioxide.

Sulphurous anhydride—Sulphurous acid—Sulphurous oxide—SO_2.—Sulphur dioxide exists in volcanic gases, and in solution in some natural waters.

It is prepared by burning sulphur in air. This method is adopted when the gas is required as a disinfectant, and in some sulphuric acid factories.

By roasting iron pyrites in a current of air, in most sulphuric acid factories.

During the combustion of coal or coke containing sulphur, and of coal-gas contaminated with carbon disulphide.

By heating strong sulphuric acid with copper turnings:

$$2SO_4H_2 + Cu = SO_4Cu + 2H_2O + SO_2.$$

The acid is brought in contact with the metal and heated until the action begins, after which the heat is moderated, or, if the action become too violent, withdrawn entirely. This is the method followed for obtaining the gas in the laboratory. The product must be passed through a small quantity of water. The same reduction of sulphuric acid is accomplished by other substances, such as sulphur, carbon, mercury, and silver. According to the United States and British Pharmacopœias, charcoal is to be used.

Sulphur dioxide is a colorless gas, having a suffocating odor (that of burning sulphur matches), and a disagreeable and persistent taste. Sp. gr. 2.234 A—32.25 H. It may be easily liquefied at —10°, forming a colorless, mobile, transparent liquid, which solidifies at —75° and boils at —8°. By a rapid evaporation of the liquid, a temperature of —65° is obtained. It is very soluble in water, which, at 15°, dissolves more than forty times its volume. It is also very soluble in alcohol.

Sulphur dioxide is not a supporter of combustion, nor will it burn in air. When heated in contact with hydrogen, it is decomposed with formation of water and separation of sulphur. In presence of nascent hydrogen, however, hydrogen sulphide and water are formed.

Water not only dissolves the gas, but forms with it a true hydrate, SO_3H_2, which exists in the solution. A hydrate of this acid, crystalline, fusible at +4°, and having the composition $SO_3H_2 + 8H_2O$, has been separated. While, therefor, the name sulphurous *acid* is incorrect as applied to the gas, it is perfectly applicable to the solution. Such a solution is

officinal under the name *Acidum sulphurosum* (U. S., Br.) (U. S. sp. gr., 1.035—Br. sp. gr. 1.04; both nearly saturated at the ordinary temperature).

It is a valuable reducing agent, for which purpose it is frequently used, either in the gaseous form or in solution. Its deoxidizing power is due to the absorption of oxygen by the sulphurous acid to form sulphuric acid:

$$SO_2H_2+O=SO_4H_2;$$
$$SO_2+H_2O+O=SO_4H_2.$$

It decolorizes vegetable substances, without, however, permanently destroying the pigment; for if an organic substance, bleached by sulphur dioxide, be washed with dilute sulphuric acid, the color is restored. Its bleaching power is utilized in the manufacture of straw, silk, and woollen goods. It is probable that this decoloration is due to an oxidation of sulphurous acid at the expense of the oxygen of water, the nascent hydrogen uniting with the coloring-matter to form a colorless compound, as indigotine is converted into white indigo by the action of reducing agents. It is also used as a disinfecting and deodorizing agent—probably behaving toward other organic matters as toward the pigments. Its chief value, however, for this purpose is in the destruction of hydrogen sulphide, which it brings about with formation of water and pentathionic acid, and liberation of sulphur:

$$4SO_2+3H_2S=2H_2O+S_5O_6H_2+S_2.$$

In this case it is not a reducing, but an oxidizing agent.

Sulphur dioxide and chlorine combine directly under the influence of sunlight to form a liquid having the composition SO_2Cl_2, the chloride of the divalent radical sulphuryl $(SO_2)''$, which also exists in sulphuric acid, and which may be considered as existing free in sulphur dioxide, as carbonyl $(CO)''$ exists free as carbonic oxide.

Corresponding to sulphurous acid, which is dibasic, are salts known as *sulphites*.

Although poisonous when inhaled in the concentrated form, it can only be regarded as annoying when largely diluted with air; moreover, individuals become quickly habituated to inhaling air containing comparatively large quantities of this gas. A delicate reagent for the presence of sulphur dioxide is obtained by moistening paper, impregnated with starch paste, with a solution of iodic acid; a mere trace of the gas, 1 to 3,000, in air, is sufficient to reduce the iodic acid, when the liberated iodine produces a blue color with the starch.

Sulphur Trioxide.

Sulphuric anhydride—Sulphuric oxide, SO_3.—Although formed by the direct union of sulphur dioxide and oxygen, at 250°–300°, and in the presence of spongy platinum, this substance is more easily obtained from Nordhausen sulphuric acid (*q. v.*), by distillation at a temperature below 100°, and collection of the vapors in a condenser cooled by a mixture of ice and salt.

It appears in the form of white, silky needles. It is capable of exist-

ing in two forms, which differ from each other in their fusing and boiling points. It has a great tendency to unite with water to form sulphuric acid—

$$SO_3 + H_2O = SO_4H_2,$$

and when exposed to the air it gives off white fumes of that substance, formed by union with atmospheric moisture. When it is thrown into water a hissing sound is observed, and there is a marked elevation of temperature. When perfectly pure it does not redden dry, blue litmus paper; nor has it any corrosive action upon animal tissues until, by absorption of moisture, it is converted into sulphuric acid.

Berthelot has described another oxide of sulphur, having the composition S_2O_7—an unstable, crystalline body, formed by the union of sulphur dioxide and oxygen, under the influence of silent electric discharges.

Oxacids of Sulphur.

These compounds form an extended series, some of the terms of which are very important industrial products. They may be divided into two groups, some of the members of which are known only in combination.

SO_2H_2 Hydrosulphurous acid.	$S_2O_6H_2$ Dithionic acid.
SO_3H_2 Sulphurous acid.	$S_3O_6H_2$ Trithionic acid.
SO_4H_2 Sulphuric acid.	$S_4O_6H_2$ Tetrathionic acid.
	$S_5O_6H_2$ Pentathionic acid.
$S_2O_3H_2$ Hyposulphurous acid.	
$S_2O_7H_2$ Pyrosulphuric acid.	

It is unfortunate that the name hyposulphurous acid (hyposulphites), should have been applied and retained by usage, to the compound $S_2O_3H_2$, as it properly belongs to SO_2H_2; discovered by Schützenberger in 1869. The so-called hyposulphurous acid may be considered as formed by the union of two molecules of SO_2H_2, with separation of a molecule of water; or as sulphuric acid in which one atom of oxygen has been replaced by an atom of sulphur.

Hydrosulphurous Acid—SO_2H_2.

Is only known in solution, in which form it is obtained by the action of zinc upon sulphurous acid in solution. It is an unstable body, and a powerful bleaching and deoxidizing agent. Upon its deoxidizing power Schützenberger and Risler have based a process for the quantitative determination of oxygen, admirably adapted for use in analysis of blood.*

Sulphuric Acid—SO_4H_2.

This acid, or rather the commercial product containing it, is manufactured in enormous quantities, and may be said to be the basis of chemical industry, as there are but few processes of chemical technology into some part of which it does not enter.

* Bull. Soc. Chim. Paris, xix., 152; xx., 145.

It was known to the earlier alchemists as *spirits of Roman vitriol;* they obtained it by the distillation of ferrous sulphate, a method still followed for the manufacture of the so-called Nordhausen acid (*q. v.*).

The method by which the commercial acid is now obtained is the result of gradual improvement, through a period of time beginning in the early part of the seventeenth century. In its present form it may be divided into two parts: 1st, the formation of a dilute acid; and 2d, the concentration of this product.

The first part is carried on in immense chambers of timber, lined with lead, and furnishes an acid having a specific gravity of 1.55, and containing sixty-five per cent. of true sulphuric acid, SO_4H_2. Into these leaden chambers sulphur dioxide, obtained by burning sulphur or by roasting pyrites, is driven along with a large excess of air. In the chambers it comes in contact with nitric acid, at the expense of which it is oxidized to sulphuric acid, while nitrogen tetroxide (red fumes) is formed:

$$SO_2+2NO_2H=SO_4H_2+2NO_2.$$

Were this the only reaction, not only would the cost of sulphuric acid be much greater than it is, but the disposal of the red fumes would offer serious obstacles to its manufacture. To avoid these difficulties, a second reaction is resorted to. Water in the form of steam, or of fine spray, is discharged into the chambers, and, coming in contact with the nitrogen tetroxide, converts part into nitric acid and part into nitrogen dioxide:

$$3NO_2+H_2O=2NO_2H+NO.$$

The nitrogen dioxide, in contact with the oxygen of air carried into the chamber, forms nitrogen tetroxide—

$$NO+O=NO_2,$$

which in turn yields more nitric acid. These series of changes go on continuously, the supply of sulphur dioxide and water being carefully regulated to the required proportions, and the nitric acid acting merely as a carrier of oxygen from the air to the acid.

The acid is allowed to collect in the chambers until it has the sp. gr. 1.55, when it is drawn off. This chamber acid, although used in a few industrial processes, is not yet strong enough for most purposes. It is concentrated, first by evaporation in shallow leaden pans until its specific gravity reaches 1.746; at this point it begins to act upon the lead, and is transferred to platinum stills, where the concentration is completed.

The product is of three grades, according to the extent to which the concentration has been carried: sp. gr. 1.833=93 per cent., SO_4H_2; sp. gr. 1.840=98 per cent., SO_4H_2; and sp. gr. 1.840=99½ per cent., SO_4H_2.

The commercial acid is an oily liquid, having a more or less pronounced brown tinge, and is known as *oil of vitriol.* It still contains many impurities, from which it is partially freed by distillation in glass, the product being the so-called C. P., or chemically pure acid, which is, however, rarely so.

The pure acid is a colorless, oily liquid; sp. gr. 1.842 at 12°; solidifies at 10.5°, and boils at 338°, although ebullition seems to begin at 290°. It is odorless, intensely acid in reaction and in taste, and highly corrosive.

The specific gravity varies with the amount of water, as shown in the following table:

DENSITIES OF SOLUTIONS OF SULPHURIC ACID AT +15°, AFTER J. KOLB.

Degree Baumé.	Specific gravity.	SO_3 per 100.	SO_4H_2 per 100.	Degree Baumé.	Specific gravity.	SO_3 per 100.	SO_4H_2 per 100.	Degree Baumé.	Specific gravity.	SO_3 per 100.	SO_4H_2 per 100.
0	1.000	0.7	0.9	23	1.190	21.1	25.8	46	1.468	46.4	56.9
1	1.007	1.5	1.9	24	1.200	22.1	27.1	47	1.483	47.6	58.3
2	1.014	2.3	2.8	25	1.210	23.2	28.4	48	1.498	48.7	59.6
3	1.022	3.1	3.8	26	1.220	24.2	29.6	49	1.514	49.8	61.0
4	1.029	3.9	4.8	27	1.230	25.3	31.0	50	1.530	51.0	62.5
5	1.037	4.7	5.8	28	1.241	26.3	32.2	51	1.540	52.2	64.0
6	1.045	5.6	6.8	29	1.252	27.3	33.4	52	1.563	53.5	65.5
7	1.052	6.4	7.8	30	1.263	28.3	34.7	53	1.580	54.9	67.0
8	1.060	7.2	8.8	31	1.274	29.4	36.0	54	1.597	56.0	68.6
9	1.067	8.0	9.8	32	1.285	30.5	37.4	55	1.615	57.1	70.0
10	1.075	8.8	10.8	33	1.297	31.7	38.8	56	1.634	58.4	71.6
11	1.083	9.7	11.9	34	1.308	32.8	40.2	57	1.652	59.7	73.2
12	1.091	10.6	13.0	35	1.320	33.9	41.6	58	1.671	61.0	74.7
13	1.100	11.5	14.1	36	1.332	35.1	43.0	59	1.691	62.4	76.4
14	1.108	12.4	15.2	37	1.345	36.2	44.4	60	1.711	63.7	78.1
15	1.116	13.2	16.2	38	1.357	37.2	45.5	61	1.732	65.2	79.9
16	1.125	14.1	17.3	39	1.370	38.3	46.9	62	1.753	66.7	81.7
17	1.134	15.1	18.5	40	1.383	39.5	48.3	63	1.774	68.7	84.1
18	1.142	16.0	19.6	41	1.397	40.7	49.8	64	1.796	70.6	86.5
19	1.152	17.0	20.8	42	1.410	41.8	51.2	65	1.819	73.2	89.7
20	1.162	18.0	22.2	43	1.424	42.9	52.8	66	1.842	81.6	100.0
21	1.171	19.0	23.3	44	1.433	44.1	54.0				
22	1.180	20.0	24.5	45	1.453	45.2	55.4				

When the vapor of sulphuric acid is heated to redness, it is decomposed into oxygen, water, and sulphur dioxide. It is also reduced, with formation of sulphur dioxide, by many substances, such as sulphur, phosphorus, carbon, mercury, copper, and silver.

Sulphur trioxide unites with water to form at least three definite hydrates: one, the compound $S_2O_7H_2$, which will be considered below; another, the so-called monohydrated acid, SO_4H_2, or, true sulphuric acid; and a third, sometimes called the bihydrated acid, having the composition $SO_4H_2+H_2O$, which crystallizes in large prisms, fusible at +8.5°; sp. gr. 1.788.

When sulphuric acid is mixed with water, there is an elevation of temperature which amounts to 100° when four volumes of acid are mixed with one volume of water. The tendency of sulphuric acid to absorb water is such that it is frequently used as a drying agent, absorbing water from the surrounding air or from gases which are caused to bubble through it. For the same reason it is unsafe to leave the acid in a vessel exposed to the air, as it is liable to absorb moisture to such an extent that by increase of bulk it overflows. When mixtures of acid and water are to be made, the acid should be added to the water (in a vessel of thin glass).

Owing to its affinity for water, sulphuric acid destroys many organic

substances, removing from them the elements of water, and, in the case of the carbohydrates, leaving a residue of carbon.

Sulphuric acid is a powerful dibasic acid.

The presence of sulphuric acid or of a soluble sulphate may be detected by the formation of a white precipitate of barium sulphate with chloride or nitrate of barium in an *acid* solution. This precipitate, when dried, mixed with charcoal and strongly heated, is converted into barium sulphide; which, when moistened with hydrochloric acid, gives off hydrogen sulphide, recognizable by the blackening of paper moistened with solution of lead acetate.

There are three varieties of sulphuric acid used in pharmacy. The *Acidum sulphuricum* (U. S., Br.), the so-called C. P. acid, having a specific gravity of 1.842, used only in the preparation of other pharmaceutical preparations; *Acidum sulphuricum dilutum* (U. S., Br.), the last mentioned diluted with water to sp. gr. 1.082 U. S., containing 11.9% SO_4H_2 (sp. gr. 1.094, Br., containing about 13% SO_4H_2); *Ac. sulph. aromaticum* (U. S., Br.), containing about the same proportion of acid as the Ac. sulph. dil., U. S.

Impurities.—The commercial acid is so charged with foreign substances as to render it entirely unfit for medicinal and for any but the coarsest chemical uses. Even the C. P. acid is obtained sufficiently free from certain impurities for toxicological analysis only with considerable difficulty. The principal impurities are the following: lead, recognizable by the production of cloudiness when the acid is diluted with water, lead sulphate being less soluble in dilute than in concentrated acid. Potassium sulphate, fraudulently added to increase the specific gravity, may be detected by evaporating to dryness. Organic matter, communicating a dark color to the acid. These impurities do not occur in the C. P. acid. An acid to be used in toxicological analysis should respond favorably to the following tests: it should be perfectly colorless, even after dilution with four volumes of water and treatment with hydrogen sulphide. The residue of its evaporation should be insignificant in quantity; and when moistened with a few drops of water, it should give no color with solution of potassium ferrocyanide. At least two fluid ounces, diluted with water, should give *no* arsenical stain in a Marsh apparatus, with pure zinc, during a heating of two hours (see p. 129). For certain purposes it is necessary to have an acid free from the oxides of nitrogen; such an acid cannot be bought, and can only be obtained by careful distillation of the purest purchasable acid, to which ammonium sulphate has been added, and the collection separately of those parts of the distillate which give *no* color with a solution of brucia.

Action on the Economy.

Although it is possible that sulphuric acid, taken in the diluted form in sufficient quantity, and during a sufficiently extended period of time, may act as a true poison in diminishing or destroying the alkaline reaction of the circulating fluids, we have no record of serious consequences resulting from its *poisonous* action. When, however, it comes in contact with any tissue, whether external or internal, in the concentrated or even moderately diluted form, it is one of the most active of corrosives; and cases are of frequent occurrence in which "death or serious bodily harm" have resulted from its being taken by suicides, or taken or admin-

istered by mistake. It is rarely administered with murderous intent, although it is very frequently thrown upon the body, with design to destroy the clothing or disfigure the person. The action of the acid is to destroy (to disorganize) any organic substance with which it may come in contact, and is therefor immediate. The majority of cases terminate fatally, either within a few hours, from corrosion and perforation of the œsophagus and stomach; or, exceptionally, from passage of the acid into the air-passages, and consequent asphyxia; or, weeks or months after the ingestion of the acid, from starvation, due to destruction of the mucous surfaces of the alimentary canal, or closure of the pyloric orifice of the stomach (secondary effects, improperly called "chronic poisoning").

The treatment consists in neutralizing the acid as quickly as possible, by the administration of slacked lime, or preferably, of magnesia, and in supplying materials for nutrition per rectum. The administration of such substances as white of egg, oil, etc., is mere waste of time. The use of the stomach-pump, when sulphuric acid or any corrosive has been taken, is liable to make matters worse by perforating the weakened walls of the œsophagus or stomach.

The detection of sulphuric acid in the body after death is rarely called for; when it is, it can only be accomplished by a quantitative analysis.

Within a few years the practice of "vitriol-throwing" has become quite prevalent, and the physician may be called upon to state whether stains upon the clothing or person are or are not produced by this acid. Fabrics moistened by the acid are corroded and fall to pieces readily. If dyed of a dark color, a stain is produced which is brick-red when fresh and brownish when old; if not too old, it is removed when moistened with ammonium hydrate, which also removes stains of hydrochloric acid (distinguishable by being of a brighter red), but not those of nitric acid, which are brownish yellow in color.

Hyposulphurous Acid—$S_2O_3H_2$,

Has not been isolated; the corresponding salts, hyposulphites, are used in medicine and in the arts.

Pyrosulphuric Acid.

Fuming sulphuric acid—Nordhausen sulphuric acid—Disulphuric hydrate—$S_2O_7H_2$—contained in the product known as Nordhausen oil of vitriol, obtained by distillation of ferrous sulphate. If the first portions of this distillate be separated, they become solid at the ordinary temperature, and by repeated fusions, crystallizations, and draining of the crystals, a substance is finally obtained having the above composition, and fusing at 35°. It forms salts called pyrosulphates or disulphates.

The commercial Nordhausen acid is a brown, oily liquid, fuming when exposed to the air, solidifying when cooled to 0°, and giving off SO_4H_2 and SO_3 when heated. It is used in the arts, in the manufacture of certain coloring matters (alizarin, eosin), and as a solvent for indigo (sulphindigotic acid).

The series of thionic acids have as yet only a theoretical interest. *Dithionic* or *hyposulphuric acid*—$S_2O_6H_2$—is obtained as an unstable,

acid, syrupy liquid, sp. gr. 1.437, by passing sulphur dioxide through water holding manganese dioxide in suspension, decomposition with barium sulphide and sulphuric acid in proper proportion, and subsequent concentration in vacuo.

Trithionic acid, $S_3O_6H_2$—obtained in a very acid, bitter, odorless solution by passing sulphur dioxide through a solution of potassium hyposulphite, decomposing the solution of potassium trithionate, thus formed with tartaric, perchloric, or hydrofluosilicic acid, and concentrating the solution in a dry vacuum.

Tetrathionic acid, $S_4O_6H_2$—obtained in acid, colorless, odorless solution, by decomposing a solution of its barium salt, prepared by the action of iodine upon barium hyposulphite.

Pentathionic acid, $S_5O_6H_2$—obtained in aqueous solution by the action of hydrogen sulphide upon solution of sulphurous acid.

Compounds of Sulphur, with Chlorine, Bromine, and Iodine.

There is but one chloride of sulphur, S_2Cl_2, which is formed when dry chlorine is passed through an excess of sulphur heated to fusion; the product is purified by redistillation. An oily, yellow fluid, boiling at 136°, having a disagreeable, nauseous odor and fuming when exposed to the air. It dissolves sulphur abundantly, and such a solution, mixed with benzine or with carbon disulphide, is used in the vulcanization of rubber. Other chlorides of sulphur SCl_2, and SCl_4, have been described, but their existence is problematic.

A single bromide of sulphur, S_2Br_2, is known as a very unstable red liquid, boiling at 215°, and formed by the action of bromine upon sulphur dioxide in the presence of phosphorus trichloride.

An iodide of sulphur, S_2I_2, is formed as a steel-gray, crystalline mass, fusible at 60°, when equivalent quantities of sulphur and iodine are gently heated to fusion together, *Sulphuris iodidum* (U. S., Br.), or by the action of sulphur chloride upon ethyl iodide. Other ill-defined iodides have been described.

SELENIUM AND TELLURIUM.

Se 79.5
Te 128

Selenium.—Discovered in 1817 by Berzelius; an element existing in very small quantities and in limited distribution in combination with sulphur, and as the selenides of lead, mercury, silver, and copper. It is capable of existing in two allotropic forms. In its compounds it closely resembles sulphur. Neither the element nor any of its compounds has been utilized in the arts or in medicine.

Tellurium.—One of the least common of the elements; discovered in 1782, by Müller, of Reichenstein. It exists in nature uncombined, and as the tellurides of bismuth, lead, silver, antimony, nickel, and gold.

It is a solid body, having a metallic lustre, fusible at about 500°, and capable of distillation in an atmosphere of hydrogen. In its chemical properties and compounds it resembles sulphur and selenium. Its use in medicine has been attempted, but abandoned.

III. NITROGEN GROUP.

NITROGEN	N	14
PHOSPHORUS	P	31
ARSENIC	As	75
ANTIMONY	Sb	122

The elements of this group are either trivalent or pentavalent. With hydrogen they form non-acid compounds composed of one volume of the element in the gaseous state with three volumes of hydrogen, the union being attended with a condensation of volume of one-half. Their hydrates are acids containing one, two, three, or four atoms of replaceable hydrogen.

Bismuth, frequently classed in this group, is excluded, owing to the existence of the nitrate $(NO_3)_3$, Bi. The relations existing between the compounds of the elements of this group are shown in the following table:

NH_3, Ammonia.	N_2O, Nitrogen monoxide.	NO, Nitrogen dioxide.	N_2O_3, Nitrogen trioxide.	NO_2, Nitrogen tetroxide.	N_2O_5, Nitrogen pentoxide.
PH_3, Hydrogen phosphide.			P_2O_3, Phosphorus trioxide.		P_2O_5, Phosphorus pentoxide.
AsH_3, Hydrogen arsenide.			As_2O_3, Arsenic trioxide.		As_2O_5, Arsenic pentoxide.
SbH_3, Hydrogen antimonide.			Sb_2O_3, Antimony trioxide.		Sb_2O_5, Antimony pentoxide.
					NO_3H, Nitric acid.
PO_2H_3, Hypophosphorous acid.	PO_3H_3, Phosphorous acid.	PO_4H_3, Phosphoric acid.	$P_2O_7H_4$, Pyrophosphoric acid.		PO_3H, Metaphosphoric acid.
	AsO_3H_3 Arsenious acid.	AsO_4H_3, Arsenic acid.	$As_2O_7H_4$, Pyroarsenic acid.		AsO_3H, Metarsenic acid.
		SbO_4H_3, Antimonic acid.	$Sb_2O_7H_4$, Pyroantimonic acid.		SbO_3H, Metantimonic acid.

NITROGEN.

N.....14

First recognized as the irrespirable constituent of atmospheric air by Dr. Rutherford, of Edinburgh, in 1772, and by him called *aer mephiticus;* subsequently "rediscovered" by Scheele and Lavoisier, in 1777, and named

azote (ἀ ζωὴ) by the latter, a name still retained by French chemists. The name nitrogen (*νίτρον γένεσις*) was given subsequently by Chaptal.

It exists in nature uncombined as one of the constituents of atmospheric air, and in combination in mineral substances, as well as in some of the most important of organic bodies.

It is usually obtained from atmospheric air by removal of oxygen, as by burning phosphorus in a limited quantity of air, or by passing a slow current of air over copper heated to redness. As thus obtained, nitrogen is contaminated with other constituents of air, carbon dioxide, etc.; to obtain it in a state of purity, recourse is had to decomposition of ammonium hydrate by chlorine gas, care being had, however, that the ammoniacal compound is always present in excess, to avoid the formation of the highly explosive nitrogen chloride.

It is a tasteless, odorless, colorless gas, non-combustible, and not a supporter of combustion; sp. gr. 0.972A—14.041H; very sparingly soluble in water and in alcohol.

Nitrogen is very slow to enter into combination with other elements, and its compounds, once formed, are, as a rule, very prone to decomposition, either sudden with explosion, or gradual by putrefaction. Nitrogen and oxygen are capable of uniting directly under the influence of electric discharges. Direct union of nitrogen and hydrogen does not take place under ordinary conditions, but does under the influence of electric discharges, and during the decomposition of organic substances containing nitrogen. Nitrogen exerts no poisonous action when inhaled; an animal in an atmosphere of pure nitrogen dies from simple lack of oxygen. This gas has been put to no use in the arts, and is used in the laboratory only when an atmosphere possessing the negative qualities of nitrogen is desired.

Atmospheric Air.

By the alchemists, and until the latter half of the seventeenth century, air was supposed to be an elementary substance, its compound nature being first recognized by Mayow in his *Tractatus quinque medico-physici*, published in 1669. It was not, however, until 1770 that Priestley repeated and amplified the researches interrupted by the death of Mayow, nearly a century before. Subsequently the labors of Scheele, Lavoisier, and Rutherford added largely to the value of Priestley's and of Mayow's discoveries.

The composition of atmospheric air, under varying conditions of time, location, temperature, pressure, etc., has been the subject of many and elaborate investigations, which have shown that, notwithstanding the fact that air is a mere mechanical mixture, and notwithstanding the additions to and subtractions from its constituent gases, to which it is subjected by the processes of animal and vegetable life, its composition is nearly constant; slight variations only having been observed in the quantity of gases present in small amounts. Leaving these out of consideration, air is composed of:

	By volume.	By weight.
Oxygen	20.93	23
Nitrogen	79.07	77

The mean of two hundred and thirty-three analyses by Regnault, of air from different locations, gives as the proportion of oxygen in volume:

20.953; the extremes being 20.908 and 20.999. When air is dissolved in water the proportion of its constituent gases does not remain the same, as would be the case were it a definite compound; but each gas is dissolved according to its own solubility in water. As oxygen is more soluble than nitrogen, dissolved air is richer in the former gas than is that existing free. According to Bunsen, water saturated with air at 13° contains:

Oxygen	34.73
Nitrogen	65.27

Besides these two main constituents, air contains about four to five thousandths of its bulk of other substances: vapor of water, carbon dioxide, ammoniacal compounds, hydrocarbons, ozone, oxides of nitrogen, and solid particles held in suspension.

Vapor of water.—The proportion of vapor of water in the atmosphere varies greatly at different times, and at varying distances from large bodies of water, the air being rarely completely saturated with water and never entirely free therefrom. Atmospheric moisture is either visible, as in fogs, clouds, etc.; or invisible, in solution, as it were. The quantity of water which air is capable of thus holding in solution is greater at high than at low temperatures and pressures. Any sudden diminution of temperature or pressure of an air holding a large quantity of moisture will bring about the condensation of the moisture into droplets. Dew and hoar-frost are thus produced by diminution of temperature during the night. Clouds are formed by the air rising from the surface, becoming colder in the upper atmospheric layers, and being there under less barometric pressure than at the surface, where it has become charged with moisture. Frequently also a current of cold air, mixing with air that is warmer and charged with moisture, determines the formation of clouds or fogs, the latter being simply clouds near the surface.

The actual amount of water in air is determined by passing a known volume of air through tubes filled with some drying agent, such as calcium chloride, whose increase of weight represents the weight of water contained in the volume of air acted upon. The amount of water in the atmosphere varies from three to sixteen volumes of vapor per thousand of air; being, as a rule, less in winter than in summer; less in northern latitudes than in the tropics; less in inland regions than in the vicinity of large bodies of water; less at high altitudes than at the sea-level; and less in cleared than in wooded districts. Near the sea-shore the air contains more moisture when the wind blows from the sea than when it blows in the opposite direction.

The degree of dampness of the air does not depend upon the absolute quantity of watery vapor which it contains, but upon the proportion existing between that quantity and the amount of water which the air could hold if saturated with moisture at the same temperature and pressure; a proportion which is known as the *fraction of saturation* of the air; or its hygrometric condition, determined by instruments called *hygrometers, hygroscopes*, or *psychrometers*. While the air in winter is usually more *damp* than in summer, it contains an absolute quantity of water, less in the winter than in the summer; but, being in the former season more nearly saturated, its tendency to precipitate the moisture is greater; while during the summer months, on the other hand, the air, although containing more aqueous vapor than in winter, is, at the reigning

temperature, less nearly saturated, and consequently more capable of exerting a drying influence by taking up a further quantity of water.

The degree of saturation influences the body temperature materially by impeding or promoting evaporation from the surface, which is greater the less near the air is to its point of saturation. Heat is, therefor, more oppressive when the air is moist than when it is dry. Life may be, for the same reason, maintained at a much higher temperature if the air be dry than if it be moist.

When dwellings are heated artificially in winter, the air should be charged with vapor of water by placing a pan containing water on the stove or in the air-box of the furnace; for, although the actual amount of moisture is not diminished, the degree of saturation is, and the air in consequence becomes dry and close unless vapor of water be added.

Carbon dioxide.—The quantity of atmospheric carbon dioxide varies from three to six parts in ten thousand by volume, the average in the country being four in ten thousand. The amount is greater in cities, or in the neighborhood of natural or artificial sources of the gas, than in the open country; on land greater during the night than during the day. At sea the reverse is the case, the difference being due to the removal of carbon dioxide by plants under the influence of sunlight in the one case, and to the greater solubility of the gas in cold than in warm water in the second. The quantity is also greater in the atmospheric layers nearest the earth than in those at greater elevations (see p. 237).

Other substances contained in air—Ammoniacal compounds.—Air contains small quantities of ammoniacal salts, carbonate, nitrate, and nitrite, the products of the decomposition of animal and vegetable substances. They are present in very small amount, not exceeding a few millionths, and are taken up by plants, by which they are assimilated. Frequently in cold, dry weather, ammonium nitrate will be found condensed as a snow-white crust on the sides of ventilators from stables, urinals, etc.

Hydrocarbons.—In the air of cities undetermined hydrocarbons have been detected to the maximum extent of 0.0001 part by volume. In the air of swampy places the proportion is greater (see Marsh-gas).

Nitric and nitrous acids exist in combination, usually with ammonia. They are produced either by the oxidation of combustible substances, or by direct union of nitrogen with vapor of water under the influence of electric discharges. Rain-water falling during thunder-showers contains comparatively large quantities of ammonium nitrate.

Solid particles in suspension in air are exceedingly diverse in their nature. Inorganic salts, notably chloride of sodium, are especially abundant in air in the vicinity of salt water, and rarely is air so free from this salt that the flame of a Bunsen burner, when examined spectroscopically, does not show the sodium lines.

Minute particles of the most heterogeneous substances float in air as dust, and become visible in the path of a ray of sunlight. The continued inhalation of air containing large quantities of such solid particles in suspension may cause severe pulmonary disorder by mere mechanical irritation, and apart from any poisonous quality in the substance; such is the case with the air of carpeted ball-rooms, and of the workshops of certain trades, furniture-polishers, metal-filers, etc.

Air always contains varying quantities of vegetable germs, to which the phenomena of the so-called spontaneous generation are due, and concerning whose action in the propagation of disease so much has been

written and so little is known. By miasms are understood certain ill-defined, putrescible, volatile, or solid substances contained in air and evolved from unhealthy localities.

The air of confined spaces in which human beings or animals are respiring is not only deteriorated by the production of carbon dioxide and consumption of oxygen (see p. 240), but also by the discharge into it of particles of organic matter prone to putrefaction. These emanations, even when derived from healthy persons, soon render the air foul, and their removal from spaces in which many people are congregated is one of the chief functions of ventilation.

Ammonia.

Hydrogen nitride—NH_3—does not exist as such in nature.

Obtained by decomposition of ammonium chloride, sulphate, or carbonate, by slightly heating with dry slacked lime. In the laboratory, by heating aqua ammoniæ, and drying the gas by passing it through a tube containing quicklime. At ordinary temperatures and pressure it is a colorless gas, having a penetrating odor; irritating to the eyes and air-passages; sp. gr. 0.589A—8.5H.; exceedingly soluble in water, with which it enters into combination (see p. 409); at $-40°$ at the ordinary pressure, or at 10° under a pressure of six atmospheres, it forms a colorless, mobile liquid, which boils at $-33.7°$; and at $-75°$ forms a colorless, transparent, crystalline mass, having but little odor.

Ammonia is formed with difficulty by the union of its elements (see p. 95). When a mixture of hydrogen and one of the oxides of nitrogen is passed over heated platinum-sponge, reduction occurs, with formation of water and ammonia. If a mixture of sulphuric and nitric acids in proper proportion be poured upon zinc, there is no evolution of gas, although the zinc dissolves. In this reaction the hydrogen reduces the nitric acid with formation of an ammoniacal compound.

Most organic substances containing nitrogen yield an ammoniacal compound, either by dry distillation, putrefaction, or the action of vapor of water, or of the caustic alkalies.

Ammonia is decomposed—two volumes yielding one volume of nitrogen and three of hydrogen—by being heated to redness, or by the passage of the electric spark through it; by chlorine or bromine, with liberation of nitrogen (see Nitrogen Chloride); by iodine with formation of explosive compounds of iodine and nitrogen; by the alkaline hypochlorites and hypobromites.

Under ordinary conditions, ammonia is neither a supporter of combustion nor combustible; it may be made to burn, however, in an atmosphere of oxygen, and mixtures of ammonia with oxygen, with nitrogen monoxide, or with nitrogen dioxide, explode when fired by the passage through them of the electric spark.

Potassium, when heated in an atmosphere of ammonia, replaces an atom of hydrogen with formation of potassium amide, KH_2N. With silver nitrate, ammonia forms two compounds, differing from each other in the temperatures at which they are formed, and in the readiness with which they give off ammonia. With the acids ammonia unites directly to form ammoniacal salts (see p. 408).

When inhaled, ammonia produces violent irritation of the respiratory

organs, and a sense of suffocation. Care should be had in administering the vapor in fainting-fits, etc., as cases are recorded in which death has resulted from the use of too liberal doses.

Nitrogen Monoxide.

Nitrous oxide—Laughing-gas—Nitrogen protoxide, N_2O.—Discovered in 1766, by Priestley; further studied by Sir Humphrey Davy, who observed its effects upon the economy when inhaled.

Prepared by decomposing ammonium nitrate by heat:

$$NO_3(NH_4)=N_2O+2H_2O.$$

If the gas be desired pure—as it should always be when used as an anæsthetic—the ammonium salt must be pure and dry, and, especially, free from chloride, lest the gas be contaminated with chlorine. The salt should be heated, not too quickly, and the temperature maintained between 210° and 250°. Below the lower temperature the decomposition does not occur, and the salt sublimes; while, at temperatures above 250°, nitrogen dioxide and nitrogen trioxide are also formed. As an additional precaution, the gas should be caused to bubble through solutions of sodium hydrate and of ferrous sulphate, to arrest any higher oxides of nitrogen which may be formed.

Nitrogen monoxide is a colorless, odorless gas, having a sweetish taste; sp. gr. 1.527A—22H; somewhat soluble in water, more so in alcohol. Under a pressure of thirty atmospheres at 0°, it forms a colorless, mobile liquid, which boils at −87.9°, and solidifies at −100°. The liquefied gas, in suitable wrought-iron vessels, is obtainable from dental depots, and is used by dentists as a convenient source of the gas for use as an anæsthetic.

Nitrogen monoxide is decomposed by a red heat, or by the continued passage of the induction spark. It is, after oxygen, the best supporter of combustion known, being readily decomposed into a mixture of oxygen and nitrogen, in which the former gas is in larger proportion than in atmospheric air (36.36 per cent. by weight).

The action of this gas upon the economy is of medical interest, from its use as an anæsthetic, and in connection with the history of anæsthesia. Although, owing to the readiness with which nitrogen monoxide is decomposed into its constituent elements, and the nature and relative proportions of these elements, it is capable of maintaining respiration longer than any gas or mixture of gases, except oxygen or air; an animal will live for a short time only in an atmosphere of pure nitrous oxide. When inhaled diluted with air, it produces the effects first observed by Sir Humphrey Davy in 1799: first an exhilaration of spirits, frequently accompanied by laughter, and a tendency to muscular activity, the patient sometimes becoming aggressive; afterward there is loss of consciousness and complete anæsthesia. It has been much used, by dentists especially, as an anæsthetic in operations of short duration, and in one or two instances anæsthesia has been maintained by its use for nearly an hour.

A solution in water under pressure, containing five volumes of the gas, is sometimes used for internal administration.

Nitrogen Dioxide.

Nitric oxide—NO.—Discovered by Hales in 1772.
Prepared by the action of copper upon nitric acid:

$$3Cu+8NO_3H=3\,(NO_3)_2Cu+4H_2O+2NO.$$

At first the flask in which the action takes place is filled with brown fumes, which gradually disappear; the gas is not collected until it has become colorless; the acid used should not be too concentrated, and should not be allowed to become heated.

It is a colorless gas, whose taste and odor are unknown; sp. gr. 1.039A—15H; very sparingly soluble in water; more soluble in alcohol.

When mixed with oxygen or air, it immediately unites with oxygen to form the tetroxide, which appears as a reddish brown gas. When passed through a solution of ferrous sulphate, it is absorbed by the liquid, to which it communicates a dark brown or black color.

Although containing a greater proportion of oxygen than air or nitrogen monoxide, it is not as good a supporter of combustion as either of those gases; although phosphorus burns in it brilliantly, and the alkaline metals unite with its oxygen with incandescence when heated in its presence.

Nitrogen Trioxide.

Nitrous anhydride—N_2O_3.—A substance not yet isolated in a state of purity, the purest yet obtained still containing about five per cent. of the tetroxide, from which it is obtained by decomposing with water at a low temperature:

$$4NO_2+H_2O=2NO_2H+N_2O_3.$$

At ordinary temperatures it is a gas, whose properties are masked by the presence of the tetroxide; below the freezing-point of water it is a dark indigo-blue liquid, which, boiling at about 0°, suffers partial decomposition.

Nitrogen Tetroxide.

Nitrogen peroxide—Hyponitric acid—Nitrous fumes—NO_2.—Formed whenever nitrogen trioxide comes in contact with oxygen. More readily, and in a condition of greater purity, by heating dry lead nitrate to redness, when nitrogen tetroxide is given off and lead oxide remains.

Formed also indirectly when a metal is dissolved in nitric acid; and directly when nitric acid is brought in contact with a platinum surface heated to redness.

This substance is remarkable for assuming when pure the three conditions of matter within a comparatively small range of temperature; above 22° it is a gas; between that temperature and −9° it is a liquid; and below that a solid. The color of the liquid varies with the temperature, being of a light brown color at ordinary temperatures, and darkening as the point of solidification is approached. Nitrogen tetroxide is decomposed

by water with the formation of nitrous and nitric acids, and by the hydrates of the alkaline and alkalo-earthy metals, with formation of a nitrite and a nitrate.

Action on the Economy.

The brown fumes given off during many processes, in which nitric acid is decomposed, consist largely of nitrogen tetroxide, and are not only offensive, but dangerous to life. All such operations, when carried on on a small scale, as in the laboratory, should be conducted under a hood or some other arrangement, by which the fumes are carried into the open air; when, in industrial processes, the volume of gas formed becomes such as to be a nuisance when discharged into the air, it should be absorbed, either by utilizing it in the manufacture of sulphuric acid, or by causing it to be absorbed by water or an alkaline solution.

An atmosphere contaminated with brown fumes is more dangerous than one containing chlorine, as the presence of the latter is more immediately annoying, while the former only produces its full effects some time after inhalation.

Quite a number of fatal cases are recorded, usually resulting from the spilling of nitric acid and attempts on the part of the victim to prevent or repair damage caused thereby. At first there is only coughing, and it is only two to four hours later that a difficulty in breathing is felt, death occurring in ten to fifteen hours. At the autopsy the lungs are found to be extensively disorganized and filled with black fluid.

Even air containing small quantities of brown fumes, if breathed for a long time, produces chronic disease of the respiratory organs. To prevent such accidents, thorough ventilation in locations where brown fumes are liable to be formed is imperative. In cases of spilling nitric acid, safety is to be sought in retreat from the apartment until the fumes have been replaced by pure air from without.

Nitrogen Pentoxide.

Nitric anhydride, N_2O_5.—Obtained by Deville, by decomposing dry silver nitrate with dry chlorine, the operation being aided by gentle heat, and conducted in an apparatus made entirely of glass, with ground joints; or, more readily, by the removal of water from fuming nitric acid by the action of phosphorus pentoxide.

It forms prismatic crystals, which fuse at 30°, and boil at 47°. It takes up water with great eagerness, and gives off white fumes when exposed to the air, the result of its combination with water being nitric acid. Even when kept in sealed tubes at low temperatures, it decomposes slowly into oxygen and nitrogen tetroxide, the pressure of the gases formed being often sufficient to fracture the glass, although the pentoxide is not, strictly speaking, explosive. The decomposition is hastened by the action of heat or of light. Most substances which unite readily with oxygen remove that element from the pentoxide, the action being attended with the appearance of light and heat.



Nitrogen Acids.

Three of these are known to exist, either free or in combination:

Hyponitrous acid,	Nitrous acid,	Nitric acid,
NOH,	NO_2H,	NO_3H,

corresponding to the three oxides, which contain for two atoms of nitrogen an uneven number of atoms of oxygen:

$$N_2O + H_2O = 2NOH.$$
$$N_2O_3 + H_2O = 2NO_2H.$$
$$N_2O_5 + H_2O = 2NO_3H.$$

Hyponitrous acid, NOH.—Obtained by E. Divers, in 1871, as its silver salt, by the action of nascent hydrogen on sodium nitrate, and precipitation with silver nitrate; and in aqueous solution, by decomposing the silver salt with the proper quantity of hydrochloric acid; as yet only of theoretical interest.

Nitrous acid, NO_2H.—Although this acid has not yet been isolated in a state of purity, there exist, corresponding to it, a series of well-defined salts called *nitrites*, having the composition NO_2M' or $(NO_2)_2M''$.

Nitric Acid.

Acidum nitricum (*U. S.*, *Br.*)—*Aqua fortis*—NO_3H.—Known to the earlier alchemists as *aqua prima*, *aqua fortis*, or *spirits of nitre*. Its true nature was first recognized by Cavendish, in 1784. It does not exist free in nature, but is abundant and widely disseminated in its salts, the *nitrates*.

Nitric acid is formed, naturally and artificially, in the process known as *nitrification* (*q. v.*), by the decomposition of nitrogenized organic materials. It is also formed by the passage of electric discharges through a mixture of nitrogen and oxygen, a formation which takes place naturally in the atmosphere, to a limited extent. Under certain conditions, it is also formed by the action of air upon ammonia, and by the oxidation of nitrogen or of ammonia by ozone.

The nitric acid used in the arts is, however, exclusively obtained by the decomposition of the nitrates of sodium and of potassium by sulphuric acid:

$$NO_3Na + SO_4H_2 = SO_4HNa + NO_3H,$$

the decomposition being conducted by the aid of heat in cast-iron vessels, from which the vapors are conducted through earthenware bottles in which the nitric acid condenses. The acid so formed is still largely charged with brown fumes, chlorine, and sulphuric acid, from which it is separated by heating to 80°, and by rectification over lead nitrate.

The pure acid, having the composition NO_3H, is a colorless, rather heavy liquid; sp. gr. 1.52; boils at 86°; solidifies at −40°; gives off white fumes in damp air; has a strong acid taste and reaction, and destroys organic matters. The specific gravity and the boiling-point of acids of less strength differ with the amount of true nitric acid which they contain; the following table, partly from Willm's article in Wurtz' "Dict. d. Chimie," and partly from Kolb, indicates these variations.

QUANTITY OF TRUE NO_3H IN NITRIC ACIDS OF DIFFERENT DENSITIES.

Density.	Degree Baumé.	Per cent. water.	Per cent. NO_3H.	Boiling-point.
1.522	49.3	.....	100.00	86°
1.486	46.5	11.25	88.75	99°
1.452	45.0	22.22	77.78	115°
1.420	42.6	30.00	70.00	120°
1.390	40.4	36.36	63.64	119°
1.361	38.2	41.67	58.33	117°
1.338	36.5	46.16	53.84	...
1.315	34.5	50.00	50.00	113°
1.297	33.2	53.33	46.67	...
1.277	31.4	56.25	43.75	...
1.260	29.7	58.82	41.18	...
1.245	28.4	61.11	38.89	...
1.232	27.2	63.16	36.84	...
1.219	25.8	65.00	35.00	...
1.207	24.7	66.67	33.33	108°
1.197	23.8	68.18	31.82	...
1.188	22.9	69.56	30.44	...
1.180	22.0	70.83	29.17	...
1.173	21.0	72.00	28.00	...
1.166	20.4	73.08	26.92	...
1.160	19.9	74.07	25.93	...
1.155	19.3	75.00	25.00	about 104°
1.138	17.6	77.00	23.00	...
1.120	15.4	80.00	20.00	...
1.101	13.1	82.56	17.44	...
1.089	11.8	85.00	15.00	...
1.068	9.4	88.57	11.43	...
1.022	2.8	96.00	4.00	...
1.010	1.4	98.00	2.00	...

It will be observed that the boiling-point at first increases and then diminishes with dilution. If a strong acid be distilled, the boiling-point will gradually increase until it reaches about 123°, when it will remain constant, the density of distilled and distillate at this point being about 1.42; if, on the other hand, a weaker acid be taken originally, the boiling-point will rise until it reaches the same point, where it remains constant.

If heated to redness, the vapor of nitric acid is decomposed into nitrogen tetroxide, water, and oxygen. The same change takes place when the acid is exposed to light and air at ordinary temperatures; it is from this cause that nitric acid in partially filled bottles, exposed to the light, assumes a yellowish tinge. Nitric acid gives up its oxygen readily, and is thus a valuable oxidizing agent. Most of the metalloids are oxidized by it, and lower are converted into higher stages of oxidation. It also oxidizes many organic substances, and with others forms products of substitution. Copper, silver, and mercury are dissolved in nitric acid, espe-

cially under the influence of heat, with formation of nitrates and evolution of nitrogen dioxide, which, combining with atmospheric oxygen, forms brown fumes:

$$4NO_3H+3Ag=3NO_3Ag+NO+2H_2O.$$

The action between nitric acid and iron is peculiar; a weak acid dissolves the metal readily, with evolution of brown fumes; but a strong acid not only does not dissolve it, but renders it *passive*, so that when it is transferred from the strong to a weak acid no action takes place until the passive condition of the iron is destroyed by touching it with a piece of platinum wire, or by other means. When nitrogen dioxide and nitric acid come together they decompose each other, with formation of the tetroxide:

$$2NO_3H+NO=3NO_2+H_2O,$$

the tetroxide being in turn decomposed, in presence of the water of the acid, into nitric acid and the trioxide:

$$4NO_2+H_2O=2NO_3H+N_2O_3,$$

the latter being dissolved in the acid, to which it communicates a yellow, brown, or green color. An acid so charged with the trioxide, sometimes called *nitrosonitric* acid, is obtained by acting upon nitric acid, with copper or iron, or preferably, by connecting the terminals of one or more cells of a Grove battery, and removing the acid from the porous cup after the action has continued for half an hour.

Nitric acid oxidizes hydrochloric acid when brought in contact with it, with liberation of free chlorine or of compounds of chlorine, oxygen, and hydrogen. A mixture of three parts of hydrochloric acid with one part of nitric acid, both of commercial strength, is a reddish yellow liquid, known as *aqua regia*, which, in the presence of bodies capable of uniting with chlorine, is a source of that element in the nascent state.

Nitric acid occurs in commerce and in pharmacy in the following forms:

Commercial, a yellowish liquid, contaminated with oxides of nitrogen, hydrochloric acid, arsenic and other impurities, should never be used medicinally, or for any but rough chemical purposes. It is of two strengths; *single aqua fortis*, specific gravity about 1.25, and *double aqua fortis*, specific gravity about 1.4.

Fuming.—A reddish yellow fluid, of sp. gr. 1.525, highly charged with nitrogen trioxide (and tetroxide ?), more or less free from impurities, according to the care exercised in its manufacture. Used as an oxidizing agent.

C. P., or chemically pure—perfectly colorless, sp. gr. 1.522. A portion evaporated on platinum should leave no residue. When diluted with two volumes of *distilled* water it should give no cloudiness with barium chloride (sulphuric acid), or with silver nitrate (chlorine). Chloroform, when shaken with the diluted acid, should not be colored, even after the addition of a few drops of solution of hydrogen sulphide (iodine). Solution of potassium permanganate should not be decolorized when added to the dilute acid (oxides of nitrogen). When evaporated over the water-bath to small bulk, the residue, diluted with water, should not give any colored precipitate when treated with hydrogen sulphide (metals).

For analytical processes only an acid responding to these tests, or a fuming acid responding to all except those for the oxides of nitrogen, should be used. An impure acid may be purified by distilling and rejecting the first quarter of its bulk, adding to the remainder excess of silver nitrate and barium nitrate, and distilling in an apparatus of glass.

Acidum nitricum (*U. S.*, *Br.*).—An acid of sp. gr. 1.42, containing 70% NO_3H, and free from impurities other than water.

Acidum nitricum dilutum (*U. S.*, *Br.*), the last mentioned, diluted with water to sp. gr. 1.068=11.43% NO_3H (*U. S.*), or sp. gr. 1.101= 17.44% NO_3H (*Br.*).

Nitric acid should be kept in bottles completely filled and protected from the light.

Analysis—The presence of nitric acid, or of a nitrate, may be detected by the following tests:

First.—Add to the liquid an equal volume of concentrated sulphuric acid, cool, float upon the surface of the mixture a small quantity of a solution of ferrous sulphate; if nitric acid or a nitrate be present, the lower layer is after a time colored, beginning at the top, black, brown, or reddish purple, according to the quantity of acid present.

Second.—Boil in a test-tube a small quantity of hydrochloric acid containing enough solution of sulphindigotic acid to communicate a blue color; if now nitric acid or a solution of a nitrate be added, and the mixture again boiled, the color is discharged.

Third.—If acid, neutralize with an alkali, evaporate to dryness, add to the residue a few drops of sulphuric acid and a crystal of brucia; a red color is communicated to the alkaloid by nitric acid. In place of brucine, sulphanilic acid may be used.

Fourth.—Heat the suspected solution (to which, in the case of a nitrate, concentrated sulphuric acid has been added) with copper turnings in a test-tube; if nitric acid be present, brown fumes will appear, best visible by looking into the mouth of the tube.

All neutral nitrates are soluble in water; some so-called basic salts are insoluble, as bismuthyl nitrate, $NO_3(BiO)$.

Action on the Economy.

Nitric acid cannot be said to be a true poison, for, although most of the nitrates exert a poisonous action when taken internally, that action seems to be due more to the metal than to the acid radical. Nitrates have also been found to be, although in very small quantity, normal constituents of the urine.

The acid is, however, one of the most powerful of corrosives; any animal tissue with which it comes in contact is immediately disintegrated; a yellow stain, afterward turning to dirty brownish, or, if the action be prolonged, an eschar, is formed. When taken internally its corrosive action is the same as that which follows its application to the cutaneous surface, but, owing to the function of the parts, is followed by more serious results. As is the case with the other mineral acids, it is rarely administered with intent to murder, but is frequently taken by suicides, or by mistake by children or inebriates. The symptoms following its ingestion are the same as those appearing with the other corrosive acids, with the exception that the mouth and any other parts with which the acid may have come in contact, as well as shreds of detached mucous

membrane in the vomited matters, are stained yellow, which is not the case when sulphuric or hydrochloric acid has been taken.

The treatment is the same as in corrosion by sulphuric or hydrochloric acid, *i. e.*, neutralization by magnesia, or, failing that, by alkalies, as rapidly as possible, and a subsequent sustaining treatment.

Compounds of Nitrogen with Elements of the Chlorine Group.

Nitrogen chloride, NCl_3, obtained by the action of chlorine gas, in excess, upon ammonia or upon an ammonium compound, or by the electrolysis of a strong solution of ammonium chloride; usually, by confining chlorine over a solution of ammonium chloride. An oily, light yellow liquid, sp. gr. 1.653; has been distilled at 71°; but when heated to 96°, when subjected to concussion, or when brought in contact with phosphorus, spirits turpentine, alkalies, oils, or grease, etc., it is decomposed into one volume of nitrogen and three volumes of chlorine, the decomposition being attended with a violent explosion. Owing to the force which this explosion exerts, great care should be had that the conditions for the formation of nitrogen chloride should not be fulfilled. If by accident the substance be formed, the laboratory should be closed and abandoned for a few days, during which the chloride will suffer spontaneous decomposition.

Nitrogen bromide—NBr_3—has been obtained as a reddish brown, syrupy liquid, very volatile, and resembling the chloride in its properties, by the action of potassium bromide upon nitrogen chloride.

Nitrogen iodide, NI_3.—When iodine is brought in contact with ammonium hydrate solution, a dark brown or black powder, highly explosive when dried, is formed. This substance varies in composition according to the conditions under which the action occurs; sometimes the iodide alone is formed; under other circumstances it is mixed with compounds containing nitrogen, iodine, and hydrogen.

PHOSPHORUS.

P.....31

Discovered in 1669, by Brandt, of Hamburg, while searching for the philosopher's stone in urine. Brandt, however, kept his process a secret, and the discovery was subsequently repeated by Kunckel and by Boyle. In 1769, Gahn detected its existence in bones, and Scheele suggested a process for obtaining it from this source. It does not exist in nature in its elementary form, but exclusively in phosphates and in certain organic substances.

Phosphorus is obtained from bone-ash, in which it exists as tricalcic phosphate (*q. v.*); this, by treatment with sulphuric acid, is converted into the soluble monocalcic phosphate—

$$(PO_4)_2Ca_3 + 2SO_4H_2 = (PO_4)_2CaH_4 + 2SO_4Ca,$$

which is separated by solution, decantation, and evaporation, from the calcic sulphate. The phosphate is then mixed with about one-fourth its weight of powdered charcoal and sand, and dried to such an extent that about five

per cent. of water is retained. The dried mixture is introduced into clay retorts, whose beaks dip under water contained in a suitable receiver; the retorts are heated, to redness at first, and finally to a white heat. During the first portion of the heating, the monocalcic phosphate is converted, by loss of water, into the metaphosphate—

$$(PO_4)_2CaH_4 = (PO_3)_2Ca + 2H_2O,$$

and this is in turn reduced by the charcoal, while the silicon dioxide removes the calcium as silicate:

$$2(PO_3)_2Ca + 2SiO_2 + 5C_2 = 2Si\,O_3Ca + 10CO + P_4.$$

The crude product so obtained is purified either by redistillation, or by fusing it under warm water, and oxidizing the impurities with a small quantity of sulphuric acid and potassium dichromate. Finally, the phosphorus is cast into glass moulds, under water.

Phosphorus exists in two distinct allotropic conditions, which differ from each other materially in their physical properties, as well as in the activity of their chemical actions.

The *ordinary* variety, also known as white, and formerly as crystallizable phosphorus, is that obtained by the process described above. It is a colorless or yellowish, translucid solid, of about the consistency of wax. Below 0° it is brittle; it melts at 44°.3, and boils at 290° in an atmosphere not capable of acting upon it chemically, being converted into a colorless gas whose specific gravity is 4.3A—61.1 H. It gives off vapors at temperatures below its boiling-point, and when water is boiled upon it the aqueous vapors are charged with its vapor. The specific gravity of the solid is 1.83 at 10°. When exposed to the air it gives off white fumes, and the odor of ozone is observed. In the dark it produces a peculiar pale light, and to this property it owes its name of "light bearer" (φῶς-φέρω). It is insoluble in water and in alcohol, soluble in carbon disulphide, benzine, petroleum, ether, and in the fixed and essential oils. Its solutions on evaporation leave it in the form of octahedral or dodecahedral crystals, in which latter form it may also be obtained by the solidification of fused phosphorus.

The *red* variety is obtained from the white by maintaining the latter at a temperature of about 250°, for thirty-six hours or more, in an atmosphere of carbon dioxide, and washing the residue with carbon disulphide as long as anything is dissolved.

It is an odorless, tasteless solid, which does not fume when exposed to the air, and is not soluble in the solvents of the ordinary variety. Its color and density depend upon the temperature at which it was formed; it is usually brownish red, and of sp. gr. 2.1. When heated to the temperature of its formation it does not melt, but at a slightly higher temperature is converted into the white variety, which either ignites or distils according to the conditions under which the conversion occurs. The red variety may also be obtained in the crystalline form, but not as readily as white phosphorus.

Besides these two forms, there are others which are by some authors considered as distinct allotropic varieties. One of these is formed as a white crust, when the ordinary phosphorus is exposed, under water holding air in solution, to diffuse daylight. Another form, called black phosphorus, is produced when ordinary phosphorus, which has been repeatedly distilled, is heated to 70° and cooled suddenly.

One of the most prominent properties of phosphorus is the readiness with which it unites with oxygen. If ordinary phosphorus be heated in contact with air to 60°, or if it be exposed in a finely divided state to air at the ordinary temperature, it ignites and burns with a bright flame, giving off dense, white clouds of phosphorus pentoxide ; it may even be burned under water heated above its fusing-point, by causing a current of oxygen to come in contact with it. The readiness with which white phosphorus fires, and the serious nature of the burns caused by it (see below), render the greatest caution necessary in handling it ; it must always be kept under water (it is best to use boiled water and to keep the bottle in the dark) ; it should never be brought in contact with the skin except under water, and when it is to be cut, this should be done under water. If desired in a finely divided condition, it may be fused in warm water (water holding urea in solution is better than pure water) and shaken until it has solidified by the cooling of the water.

The red variety does not unite with oxygen so readily, and may be kept exposed to the air and handled with impunity. When exposed to damp air it oxidizes slowly, but does not become luminous in the dark.

Either variety unites readily with chlorine, bromine, and iodine, with formation of chlorides, bromides and iodides (*q. v.*) The union of these elements with the white variety is attended with the liberation of heat and of light. Most other elements are capable of uniting directly with phosphorus; hydrogen, nitrogen and carbon are not. Many salts are reduced by white phosphorus. When immersed in a solution of cupric sulphate the surfaces of a fragment of phosphorus became coated with metallic copper; in a solution of silver nitrate the surface of the phosphorus becomes blackened by the deposition upon it of the black silver phosphide.

Action on the Economy.

The two varieties of phosphorus differ from each other in the important particular that, while the red phosphorus is practically inert when taken internally—probably owing to its insolubility—and is but little liable to give rise to burns, the white variety is actively poisonous, and, when ignited in contact with the skin, produces very painful wounds, whose effects are serious beyond what could be expected from the mere local injury produced. A burning fragment of white phosphorus adheres tenaciously to the skin, into which it burrows in burning. One of the products of the combustion is metaphosphoric acid, which, being absorbed, gives rise to true poisoning (see p. 115). Cases are not wanting in which death has followed burns by phosphorus, of an extent which would not be serious if caused by the combustion of other substances. Burns by phosphorus should be washed immediately with dilute Javelle water, liq. sod. chlorinatæ, or solution of chloride of lime.

When taken internally, phosphorus (the ordinary variety) is one of the most insidious of poisons, and one which, on the continent of Europe, has of late years become the favorite agent in homicidal poisoning—the average number per annum of cases of criminal poisoning by phosphorus in Paris being greater than that of cases of the same nature, in which arsenic was used. Whether such cases are of frequent or rare occurrence in the United States, it is difficult to determine, from the meagre and unreliable statistics at hand. Certain it is that the number of accidental and suicidal deaths from phosphorus and "rat-poison," noted in the reports

of the New York Board of Health for the past ten years, would indicate that the toxic nature of these substances is not unknown among our population.

The substances generally used are match-heads, or "rat's bane"—the former being in the ordinary sulphur match, a mixture of potassium chloride, very fine sand, phosphorus, and a coloring matter, Prussian blue or vermilion; and the latter a paste of flour charged with phosphorus. It is not improbable that the recently introduced medicinal preparations of phosphorus may produce fatal poisoning in the future. The symptoms in acute phosphorus-poisoning appear with greater or less rapidity, according to the dose, and the presence or absence in the stomach of substances which favor its absorption. Their appearance may be delayed for days, but as a rule they appear within a few hours. A disagreeable, garlicky taste in the mouth, and heat in the stomach are first observed, the latter gradually developing into a burning pain, accompanied by vomiting of dark-colored matter, which, when shaken in the dark, is phosphorescent; low temperature and dilatation of the pupils. In some cases death follows at this point suddenly, without the appearance of any further marked symptoms; usually, however, the patient rallies, seems to be doing well, until suddenly jaundice makes its appearance, accompanied by retention of urine, and frequently delirium, followed by coma and death.

There is no known chemical antidote to phosphorus; the treatment is, therefor, limited to the removal of the unabsorbed portions of the poison by the action of an emetic, zinc sulphate or apomorphia, as expeditiously as possible, and the administration of oil of turpentine—the older the oil the better—as a physiological antidote. The use of fixed oils or fats is to be avoided, as they favor the absorption of the poison by their solvent action. The prognosis is very unfavorable.

As commercial phosphorus is usually contaminated with arsenic, the effects of the latter substance may also appear in poisoning by the former.

Analysis.—When, after a death supposed to be caused by phosphorus, chemical evidence of the existence of the poison in the body, etc., is desired, the investigation must be made as soon after death as possible, for the reason that the element is rapidly oxidized, and the detection of the higher stages of oxidation of phosphorus is of no value as evidence of the administration of the element, because they are normal constituents of the body and of the food.

The detection of elementary phosphorus in a systematic toxicological analysis is connected with that of prussic acid, alcohol, ether, chloroform, and other volatile poisons. The method adopted should be a combination of the processes of Mitscherlich, Blondlot, and Neubauer and Frezenius. Mitscherlich's process would be sufficient of itself were it not that the power of phosphorescence of phosphorus is held in abeyance by the presence of alcohol or ether, and is permanently destroyed by admixture of oil of turpentine, the last-named substance being one which is very liable to be mixed with the contents of the stomach, if the case have been recognized as one of phosphorus-poisoning before death.

The substances to be examined, usually the contents of the stomach (the other volatile poisons should be looked for first in the lungs), are diluted with water, acidulated with sulphuric acid, and heated in a flask over the sand-bath. The flask is connected by a perforated cork and a long, bent tube, with a Liebig's condenser placed in a vertical position and in absolute darkness, and so arranged as to deliver the distillate into a

suitable receiver, while through the entire apparatus a current of carbon dioxide is made to pass. The odor of the distillate is noted. If phosphorus be present, it is usually garlicky. The condenser is also observed. If at the point of greatest condensation a faint, luminous ring be observed (in the absence of *all* reflections), it is proof positive of the presence of unoxidized phosphorus; the absence, however, of that poison is not to be inferred from the absence of the luminous ring. If this fail to appear when one-third the fluid contents of the flask have passed over, the receiver is removed (its contents being reserved for the detection of the more volatile poisons), and in its place are arranged two V-tubes, or a Liebig's bulb-tube filled with *neutral* solution of silver nitrate. If phosphorus be present, either in its own form or in its lower stages of oxidation, a black deposit of silver phosphide is formed; if no blackening of the silver solution occur, the absence of phosphorus may be inferred. If blackening have occurred, the deposit is introduced into the generator of an apparatus furnishing pure hydrogen (see Zinc), which, after drying over sulphuric acid, is burned as it issues from a platinum jet. If the black deposit be silver phosphide, the inner portion of the flame will be bright green, and will exhibit the characteristic green lines of phosphorus when examined spectroscopically.

Chronic poisoning by phosphorus.—This form of poisoning, also known as the Lucifer disease, occurs among operatives engaged in the dipping, drying, and packing of phosphorus matches. Sickly women and children are most subject to it. Workmen in factories where the element itself is produced are not affected. The cause of the disorder is variously ascribed to the contamination of phosphorus with arsenic, and to the presence in the atmosphere of oxides of phosphorus and ozone. The progress of the disease is slow, and its most prominent and culminating manifestation is the destruction of one or both maxillæ by necrosis.

The frequency of the disease may be in some degree diminished by maintaining a thorough ventilation of the shops, by frequently washing the face and rinsing the mouth with a weak solution of sodium carbonate, and by exposing oil of turpentine in saucers in the workshops. By none of these methods, however, will the prevention of the disease be perfect—a result which can only be attained by abandoning the use of white phosphorus, for the manufacture of matches, entirely. The increased cost of red phosphorus is of no weight against the advantages of preventing this fearful disease, and at the same time removing from the reach of the poisoner one of the most potent and easily obtained of toxic agents.

Hydrogen Phosphides.

There exist no less than three compounds of hydrogen and phosphorus, of which the most important is the one corresponding in composition to ammonia.

Gaseous hydrogen phosphide—Phosphonia—Phosphamine—PH_3—a gaseous substance, two volumes of which contain half a volume of vapor of phosphorus and three volumes of hydrogen.

It is formed in a number of reactions, but can only be obtained in a state of purity by the decomposition of phosphonium iodide, PH_4I, by water, or by solutions of the alkalies. As thus obtained, it is a colorless gas, having a strong alliaceous odor, very sparingly soluble in water;

sp. gr. 1.134A—17.5H. It fires at about 70°, or on contact with fuming nitric acid, chlorine, bromine, or iodine.

The methods usually employed for obtaining the gas are, by heating phosphorus with a strong solution of potassium hydrate, or with thick milk of lime; or by decomposing calcium phosphide by water. When prepared by these methods the gas differs from the pure substance, in that as each bubble comes in contact with air it takes fire spontaneously, with the formation of a white ring of phosphorus pentoxide; this property it owes to the presence of traces of another compound (see below).

The impure gas is also formed during the putrefaction of organic substances containing phosphorus. The natural phenomenon of ignis fatuus, or Will o' the Wisp, is probably due to such a formation of hydrogen phosphide.

The gas is highly poisonous, even when the air contains less than one per cent. Its poisonous action is due to its oxidation at the expense of the blood-coloring matter, whose destruction produces death by asphyxia. After death the blood is found to be dark, to have a violet tinge, and to have, in a great measure, lost its capacity for absorbing oxygen.

Liquid hydrogen phosphide—P_2H_4—is the substance whose vapor communicates to PH_3 its property of spontaneously igniting on contact with air. It may be obtained by passing the gas, obtained by the decomposition of calcium phosphide by water, through a bulb-tube enclosed in a freezing mixture.

It is a colorless, heavy liquid, readily decomposable at a temperature of 30°, and by other influences which also destroy the spontaneous inflammability of the gaseous product.

Solid hydrogen phosphide—P_4H_2.—A yellow solid, formed by the decomposition of P_2H_4, under the influence of sunlight. It is not phosphorescent, and only ignites when heated to 160°.

Oxides of Phosphorus.

These are two in number:

Phosphorus trioxide.....P_2O_3.
Phosphorus pentoxide.....P_2O_5.

Phosphorus trioxide—Phosphorus anhydride—P_2O_3—is formed, as a white solid, when phosphorus is burned in a limited supply of dry air or oxygen. When exposed to moist air it is fired by the heat developed by its union with water to form phosphorous acid.

Phosphorus pentoxide—Phosphoric anhydride—P_2O_5—is formed whenever phosphorus is caused to burn, in the absence of water, and in the presence of an excess of oxygen. It is a white, flocculent solid, which exhibits almost as great a tendency to unite with water as does the lower stage of oxidation.

When exposed to the air it absorbs moisture rapidly, with liberation of heat and formation of a highly acid liquid, which does not contain orthophosphoric acid, as we should expect from analogy, but metaphosphoric acid (*q. v.*). It is frequently used in the laboratory as a very energetic drying agent.

Phosphorus Acids.

These form a series of great interest from a theoretical point of view. The first has no corresponding oxide; the second is the hydrate of the trioxide, and the other hydrates are referable, directly or indirectly, to the pentoxide:

Hypophosphorous acid ..... PO_2H_3.
Phosphorous acid ..... PO_3H_3.
Orthophosphoric acid ..... PO_4H_3.
Pyrophosphoric acid ..... $P_2O_7H_4$.
Metaphosphoric acid ..... PO_3H.

The basicity of these acids is also of interest. While PO_3H is monobasic, and $P_2O_7H_4$ is tetrabasic, all of their hydrogen atoms being replaceable—the other three, although each containing three atoms of hydrogen, vary in basicity: PO_2H_3 is monobasic; PO_3H_3, dibasic; and PO_4H_3, tribasic.

Hypophosphorous Acid—PO_2H_3,

Is obtained as a strongly acid, colorless, syrupy liquid, by decomposing its barium salt with an equivalent quantity of sulphuric acid, filtering and concentrating the solution. It may also, with proper precautions, be obtained in the crystalline form. It is quite unstable, and, when exposed to the air, is oxidized into a mixture of phosphorous and phosphoric acids. Its salts are more stable, and some are used in medicine; they have the composition PO_2H_2M' or $(PO_2H_2)_2M''$.

Phosphorous Acid—PO_3H_3,

Is best prepared by the decomposition of phosphorus trichloride by water, according to the equation:

$$PCl_3+3H_2O=PO_3H_3+3HCl.$$

The hydrochloric acid formed is driven off by evaporation and by exposure over quicklime. The product is finally concentrated over sulphuric acid. It is also formed by exploding a mixture of phosphonia and oxygen, in the proportion of two volumes of the former to three volumes of the latter. It is a syrupy and highly acid liquid, readily decomposable by heat. It is an energetic reducing agent, taking up oxygen to form phosphoric acid. It forms salts called *phosphites*, whose composition is $PO_2HM'H$, $PO_3HM'_2$, or PO_3HM''.

It has been stated that this acid is formed in concentrated aqueous solution, when phosphorus is exposed to the slow action of moist air; but from the recent researches of P. Salzer it would seem that the solution so obtained contains a new acid, which he calls hypophosphoric acid, and to which he ascribes the formula PO_3H_2(?).

Orthophosphoric Acid.

Common, or tribasic phosphoric acid, PO_4H_3.—This acid, although not existing free, is widely disseminated in the three kingdoms of nature in its salts, the phosphates.

It is usually obtained by the oxidation of phosphorus by dilute nitric acid, under the influence of heat. The action is liable to become violent, and the process should always be conducted with caution; indeed, it is best to use the red phosphorus in place of the ordinary variety. This is the process adopted (with subsequent dilution) in the United States and British Pharmacopœias, to obtain the *Acid. phosph. dilutum* (see Metaphosphoric Acid), enough nitric acid being used to oxidize the phosphorus completely, and the excess being driven off by heat. The strength of the United States preparation is 10.21 per cent., PO_4H_3; sp. gr., 1.056; that of the British 14.42 per cent., PO_4H_3; sp. gr., 1.08.

In the arts phosphoric acid is now usually obtained directly from bone ash, by converting the calcium phosphate contained in them into lead or barium phosphate; the insoluble compound is removed and decomposed by hydrogen sulphide in the first case, and by sulphuric acid in proper proportion in the second.

It is also formed in other reactions, as by passing chlorine into phosphorus melted under water, when phosphorus pentachloride is formed and immediately decomposed into phosphoric and hydrochloric acids; the latter is removed by evaporation.

The concentrated acid usually is a colorless, transparent, syrupy fluid, which still contains water, and, by exposure over sulphuric acid, yields the pure acid in the form of transparent, prismatic crystals, which, on exposure to air, rapidly deliquesce, forming a highly acid, syrupy solution.

For the action of heat on this acid, see below ; for tests (see p. 114). It forms many salts, whose composition is: PO_4H_2M'; $PO_4HM'_2$; $PO_4M'_3$; $(PO_4)_2M''_3$; $(PO_4H)_2M''_2$; $(PO_4H_2)_2M''$; or $PO_4M'M''$.

Phosphoric acid made from arsenical phosphorus (commercial phosphorus is usually arsenical), is contaminated with arsenic trioxide, whose presence may be recognized by the application of Marsh's test (p. 129) to the aqueous solution. The aqueous acid should, on evaporation, leave no residue ; and should not respond to the indigo or ferrous sulphate tests for nitric acid.

Pyrophosphoric Acid—$P_2O_7H_4$.

When orthophosphoric acid (hydrodisodic phosphate) is maintained for some time at a temperature of 213°, two of its molecules unite, with loss of the elements of one molecule of water, to form a new acid—pyrophosphoric acid, so called from its igneous origin:

$$2PO_4H_3 = P_2O_7H_4 + H_2O.$$

The acid is obtained free as a transparent, vitreous, semi-crystalline, soft mass, by decomposing its lead salt with hydrogen sulphide, filtering and concentrating the filtrate. It is tetrabasic.

Metaphosphoric Acid.

Glacial phosphoric acid, PO_3H.—This acid, whose composition is similar to that of nitric acid, is formed by the action of heat, approaching redness, on either ortho- or pyrophosphoric acid. In either case there is loss of the elements of a molecule of water:

$$PO_4H_3 - H_2O = PO_3H.$$
$$P_2O_7H_4 - H_2O = 2PO_3H.$$

It is usually obtained directly from bone-ash, whose calcium phosphate is first converted into ammonium phosphate, which is then subjected to a red heat. This is the process adopted by the United States Pharmacopœia in obtaining the *Acid. phosphoricum glaciale* (see p. 115).

It appears as a white, glassy, transparent solid, odorless, and having a sour taste. Slowly deliquescent when exposed to the air, it is very soluble in water, the solution taking place quite slowly, and being accompanied by a peculiar crackling sound at intervals.

Analytical Characters of the Phosphoric Acids.

The three acids, PO_4H_3, $P_2O_7H_4$, and PO_3H, although closely related and all derived from the oxide P_2O_5, differ materially in their properties, and may, in solution of the free acids or of their salts, be distinguished from each other by the following reactions:

Orthophosphoric acid.	Pyrophosphoric acid.	Metaphosphoric acid.
	With Ammoniacal Solution of Silver Nitrate.	
A yellow precipitate.	A white precipitate.	A white precipitate.
	With Solution of Albumen.	
No effect.	No effect.	Coagulation.
	With Solution of Ammonium Molybdate in Nitric Acid.	
A yellow precipitate.	No effect.	No effect.
	With Solution of Magnesium Sulphate in the Presence of Ammonium Chloride and Hydrate.	
A white, crystalline precipitate; insoluble in ammonium hydrate, nearly so in ammonium chloride; soluble in acids.	A white precipitate; soluble in excess of phosphate or of magnesium sulphate.	No effect; or a precipitate soluble in ammonium chloride.

The last two reactions are only of value in the absence of arsenic acid.

The quantitative determination of phosphoric acid is always a tedious and delicate operation, and a discussion of the various methods proposed would fill a volume. With the simple statement that the acid is finally weighed as uranium or magnesium phosphate, the reader is referred to the works on analytical chemistry.

Action on the Economy.

Although the salts of orthophosphoric acid are important constituents of animal tissues, and give rise, when taken internally in reasonable doses, to no untoward symptoms; and although the acid itself, when ingested, may act deleteriously purely by virtue of its acid reaction, the recent researches of Gamgee, Priestley, and Larmuth, have shown that meta- and pyrophosphoric acids, even when taken in the form of neutral salts, have a distinct action (the pyro being the more active) upon the motor ganglia of the heart, producing diminution of the blood-pressure, and, in comparatively small doses, death from cessation of the heart's action. The distinction between the glacial and dilute acids of the United States Pharmacopœia becomes of importance in view of these facts.

Compounds of Phosphorus with Elements of the Chlorine Group.

The compounds of phosphorus and chlorine are three in number: PCl_3, PCl_5, and $POCl_3$.

Phosphorus trichloride—PCl_3—is prepared by passing vapor of phosphorus over mercuric chloride; or, preferably, by passing a slow current of dry chlorine over phosphorus, and purifying by distillation.

It is a colorless liquid; sp. gr. 1.61; has an irritating odor; fumes in the air; boils at 76°. On contact with water it is decomposed, with formation of phosphorous and hydrochloric acids. It is a very valuable reagent in organic chemistry.

Phosphorus pentachloride—PCl_5—is formed by the action of an excess of chlorine upon phosphorus, or upon the trichloride.

It occurs in light yellow crystals, having a powerful odor, giving off irritating vapors, and distilling at about 145°. At higher temperatures it is decomposed into $PCl_3 + Cl_2$. With a small quantity of water it forms the oxychloride, $POCl_3$, and hydrochloric acid; with a large quantity, phosphoric and hydrochloric acids. Is useful as a reagent in organic chemistry.

Phosphorus oxychloride—$POCl_3$—is formed by the action of a limited quantity of water on the pentachloride. It is a colorless liquid; sp. gr. 1.7; boils at 110°; solidifies at −10°; and has a pungent odor. Use; the same as that of the other chlorides.

With *bromine*, phosphorus forms compounds similar in composition and properties to the chlorine compounds.

With *iodine*, it forms two compounds, PI_2 and PI_3, both solid, crystalline bodies, obtained by the direct union of their elements, and both decomposed, on contact with water, into hydriodic and phosphorous acids.

Two *fluorides* of phosphorus, PF_3 and PF_5, are also known—the former liquid, the second gaseous.

Compounds of Phosphorus and Sulphur.

No less than six compounds of these elements have been described, having the formulæ: P_4S, P_2S, P_4S_3, P_2S_3, P_2S_5, P_2S_{12}. Two of these, P_2S_3 and P_2S_5, correspond to the oxides. Although of great interest in connection with theoretical chemistry, they are not of medical interest.

ARSENIC.

Arsenicum.....As.....75

Compounds of arsenic, notably the sulphides, were known to the ancients, and the element itself to the alchemists as early as the fourth century, when Geber makes mention of it.

Arsenic occurs in nature in the form of metallic arsenides, but principally as the sulphides, orpiment and realgar, and in arsenical iron pyrites, or mispickel, the last-named mineral being one of the chief sources from which it and its compounds are industrially obtained. It is also found in the elementary form in small quantities, and distributed in a vast number of other substances in quantities which, if not large, are sufficiently so to become a serious inconvenience to the toxicologist.

It is obtained for use in the arts, either by calcining mispickel and condensing the volatilized arsenic in iron tubes, or by heating a mixture of arsenious oxide and charcoal, when the former is reduced and elementary arsenic distils over.

It is a brittle, light steel-gray solid, having a metallic lustre; sp. gr. 5.75. When heated under the ordinary pressure, and without contact with air, it volatilizes without previous fusion. Under strong pressure it liquefies at a red heat. The density of its vapor is 10.2A—147.3H at 560°; 10.6A—153H at 860°. Its vapor is yellowish, and has the odor of garlic, which is probably developed during oxidation. It is insoluble in water and in other liquids which do not act upon it chemically (see p. 125).

When heated in air, arsenic is rapidly oxidized to arsenic trioxide, and ignites at somewhat below a red heat. In oxygen it burns with a brilliant white light, having a bluish tinge. In dry air it is not altered, but when exposed to damp air its surface rapidly becomes tarnished by oxidation. Its oxidation is attended by the development of an alliaceous odor. In water it is slowly oxidized, a portion of the oxide formed dissolving in the water. It unites readily with chlorine, bromine, iodine, sulphur, and most of the metals. With hydrogen it only combines when that element is in the nascent state. Sulphuric acid, when warm and concentrated, is decomposed by arsenic with formation of sulphur dioxide, arsenic trioxide, and water. Nitric acid is readily decomposed, giving up its oxygen to the formation of arsenic acid.

With hydrochloric acid, aided by heat, arsenic trichloride is formed. Arsenic is oxidized by fusion with potassium hydrate, hydrogen is given off, and a mixture of arsenite and arsenide of potassium remains, which, by increase of temperature, is converted into arsenic and potassium arsenate, the former of which volatilizes, and the latter remains.

Arsenic is used in the arts to some extent in pyrotechny, entering into the composition of the Bengal light (which should, therefor, only be used in the open air), in the manufacture of shot, and of fly-poison, and as a medicine in veterinary practice. It is poisonous (see p. 125).

Compounds of Arsenic with Hydrogen.

Two of these are known, one gaseous, the other solid.

Hydrogen arsenide, arseniuretted hydrogen, arsenia, arsenamine, AsH_3 —a compound whose composition is similar to that of ammonia and the corresponding phosphorus compound, and one which is of great practical

as well as theoretical interest. It does not exist in nature, and was discovered by Scheele.

It is formed: *First.*—By the action of water upon an alloy, obtained by fusing together a mixture of two parts of natural sulphide of antimony, two parts of cream of tartar, and one part of arsenic trioxide.

Second.—By the decomposition of the arsenides of zinc and tin (as well as of other arsenides) by dilute hydrochloric or sulphuric acid.

Third.—Whenever a reducible compound of arsenic is in the presence of nascent hydrogen:

$$As_2O_3+6SO_4H_2+6Zn=6SO_4Zn+3H_2O+2AsH_3.$$

This reaction is utilized in Marsh's test (see p. 129).

Fourth.—By the action of water upon the arsenides of the alkaline metals:

$$AsNa_3+3H_2O=3NaHO+AsH_3.$$

Fifth.—By the combined action of moisture, air, and organic matter upon arsenical pigments (see p. 125). It is a colorless gas, having a strong alliaceous odor, soluble in five volumes of water free from air. Condenses to a mobile fluid at $-40°$, does not solidify at $-110°$; sp. gr. 2.695A—38.916H.

It is not liable to spontaneous decomposition, but, in contact with air or oxygen, and moisture, its hydrogen is slowly removed by oxidation, and elementary arsenic is deposited. It is also decomposed into its elements by the passage through it of the luminous electric discharge. A mixture of dry oxygen and hydrogen arsenide remains such under ordinary circumstances, but, upon heating it, it explodes with formation of arsenic trioxide and water, three volumes of oxygen oxidizing two of the arsenical gas:

$$2AsH_3+3O_2=As_2O_3+3H_2O.$$

With a quantity of oxygen less than that indicated in the equation, elementary arsenic is deposited.

If the gas be ignited as it issues from a jet, it burns with a greenish flame, from which rises a white cloud of arsenic trioxide; if, however, the flame be cooled by the introduction of a cold body, the hydrogen is alone oxidized, the arsenic being deposited on the cold surface in its elementary form. If the gas be heated to redness as it passes through a glass tube, it is decomposed in whole or in part, hydrogen passing on and the arsenic being deposited. If hydrogen arsenide be caused to bubble through a solution of silver nitrate, that salt is decomposed; elementary silver separates as a black powder, and the solution contains arsenic trioxide. The last three reactions are utilized in Marsh's test (*q. v.*).

Chlorine decomposes the gas with great energy—the action, which is attended with considerable danger to the operator, being accompanied by an explosion, and the formation of hydrochloric acid and arsenic trichloride. Bromine and iodine act in a similar manner, but less violently.

If hydrogen arsenide be passed over solid potassium hydrate, it is partially decomposed, the potash being coated with a blackish deposit of what would seem to be elementary arsenic.

All oxidizing agents decompose the gas readily, water and arsenic

trioxide being formed by the action of the less active oxidants, and water and arsenic acid by that of the more active.

The alkaline hydrates absorb the gas, hydrogen is given off, and potassium arsenite remains in solution. Many metallic elements, when heated in an atmosphere of hydrogen arsenide, decompose it with formation of a metallic arsenide, and liberation of hydrogen.

Although hydrogen arsenide and hydrogen sulphide decompose each other to a great extent, with separation of arsenic trisulphide, the researches of Kubel, Meyers, and Otto have shown that the former gas is capable of existing, to some extent at least, in the presence of the latter; a fact which renders it necessary to use the greatest caution, in obtaining hydrogen sulphide for toxicological purposes, to use materials free from arsenic.

Arseniuretted hydrogen is exceeding poisonous (see p. 125).

Solid hydrogen arsenide.—The probable composition of this body is As_2H. It is a red-brown powder, insoluble in water and in alcohol. The only interest attaching to it is in connection with Marsh's test, in which care should be had to avoid the conditions under which it is formed. This may be done by carefully preventing the presence of any nitrate, and by moistening the zinc with a dilute solution of platinum chloride, which should be removed, and the zinc washed with pure water before the apparatus is mounted (see p. 129).

Compounds of Arsenic and Oxygen.

Only two of these are known with certainty: they are the trioxide, As_2O_3, and the pentoxide, As_2O_5, corresponding to the similar phosphorus compounds. It is probable that the gray substance, formed by the action of moist air and of water upon elementary arsenic, is a lower oxide than either of the above, possibly As_2O.

Arsenic Trioxide.

Arsenious anhydride—White arsenic—Arsenic—Arsenious acid—Acidum arseniosum (U. S., Br.)—As_2O_3.—This substance does not exist in nature, but is manufactured in large quantities industrially, either as a distinct product, by roasting mispickel, or as an incidental product in working the ores of cobalt and nickel. In either case the vapors are conducted into suitable condensing-chambers, where the solid trioxide is deposited as a white, crystalline powder, known in the arts as *flour of arsenic*. From time to time this is removed (an operation attended with no little danger to the workman employed), and purified by a second sublimation. It sometimes occurs in this last process that, owing to the presence of elementary arsenic, the iron pot in which the impure white arsenic is heated is perforated, and the contents, flowing into the fire, are volatilized into the air of the workshop, with fatal results.

Arsenic trioxide is capable of existing, and occurs in commerce, in two distinct allotropic conditions: *crystallized* or "*powdered*," and *vitreous*. When freshly resublimed, it appears in colorless or faintly yellow, transparent, vitreous masses, having no visible crystalline structure. Shortly, however, these masses become opaque upon the surface, and present the appearance of porcelain; this change, which is due to the

substance assuming the crystalline form, gradually and slowly progresses toward the centre of the mass, which, however, remains vitreous for a long time. The change is attended by the slow liberation of heat, and, if it be made to take place more rapidly, a faint light is visible in obscurity. Whenever arsenic trioxide is sublimed, if the vapors be condensed upon a cool surface, it is deposited in the form of brilliant octahedral crystals, which are larger and more perfect the nearer the temperature of the condensing surface is to 180°. The crystalline variety may be converted into the vitreous by keeping it for some time at a temperature near its point of volatilization.

The taste of arsenic trioxide is at first faintly sweet, afterward acrid, metallic, and nauseating. It is odorless; in aqueous solution (see below) it has a faintly acid reaction. The specific gravity of the vitreous variety is 3.689; that of the crystalline, 3.785.

The solubility of this substance in water and in other fluids has been the subject of many investigations. In pure water, arsenic trioxide dissolves as arsenious acid (*q. v.*); the amount dissolved depends upon the temperature, the method of making the solution, and the nature of the oxide. Thus, Bussy found that water at 13° is capable of dissolving forty grams of the vitreous oxide, but only twelve to thirteen grams of the crystalline to the litre; he found also that, by prolonged boiling with water, the crystalline variety is converted into the vitreous, or, at all events, the solubility of the two varieties becomes the same—one hundred and ten grams to the litre of boiling water. According to Taylor, cold water dissolves from one to two grams per litre only; boiling water, when poured upon the oxide and allowed to cool, dissolves 2.5 parts in one thousand; and water boiled upon the oxide, twenty-five parts per one thousand. These results are probably too low, although those for cold water agree well with the figures given by Woodman and Tidy, which represent the latest experiments upon the subject, and are given below:

	Transparent form.	Opaque form.	Fresh crystalline oxide.
1,000 parts of cold distilled water, after standing 24 hours, dissolved	1.74 parts.	1.16 parts.	2.0 parts.
1,000 parts of boiling water poured on the oxide, and allowed to stand for 24 hours, dissolved	10.12 parts.	5.4 parts.	15.0 parts.
1,000 parts of water boiled for one hour, the quantity being kept uniform by the addition of boiling water from time to time, and filtered immediately, dissolved	64.5 parts.	76.5 parts.	87.0 parts.

These results for boiling water agree better with those of Bussy than with those of Taylor.

The solution of the crystallized oxide in cold water is always very slow (the vitreous oxide dissolves more rapidly), and continues for a long time. If white arsenic be thrown upon cold water, only a portion of it sinks, the remainder floating upon the surface, notwithstanding its high specific gravity. This is due to a repulsion of the water from the surfaces of the crystals, which also accounts, to some extent at least, for its slow solution. Even after several days cold water does not dissolve all

the oxide with which it is in contact. Gmelin has shown that if one part of oxide be digested with eighty parts of water, at ordinary temperatures for several days, the resulting solution contains $\frac{1}{80}$; with 160 parts water, $\frac{1}{180}$; with 240 parts, $\frac{1}{280}$; with 1,000 parts water, $\frac{1}{1200}$; and that, even when 16,000 or 100,000 parts of water are used, a portion of the oxide remains undissolved. The same author has shown that arsenious oxide, which has remained in contact with cold water in closed vessels for eighteen years, dissolves to the extent of 1 part in 54 of water, or 18.5 parts in 1,000, which may be given as the maximum solubility of the crystallized oxide in cold water.

The power of water of holding the acid in solution, once it is dissolved, is not the same as its power of dissolving it. If a concentrated solution be made by boiling water upon the oxide and filtering hot, the filtrate may be evaporated down to one-half its original bulk without depositing any of the acid, of which this concentrated fluid now contains as much as one part in six of water, or 166.6 parts per 1,000. If a hot solution of the acid be allowed to cool, the solution will contain 62.5 parts per 1,000 at 16°, and 50 parts per 1,000 at 7°.

The solubility of the oxide in alcohol varies with the strength of the spirit and the nature of the oxide, the vitreous variety being more soluble in strong than in weak alcohol, while the contrary is the case with the crystalline, as is shown in the following table:

1,000 parts dissolve		Alcohol at 56 per cent.	Alcohol at 79 per cent.	Alcohol at 86 per cent.	Absolute alcohol.
Crystallized oxide	At 15°.....	16.80	14.30	7.15	0.25
	At the boiling-point.....	48.95	45.51	31.97	34.02
Vitreous oxide at 15°.....		5.04	5.40	.....	10.60

The presence of the mineral acids and alkalies, ammonia and ammoniacal salts, alkaline carbonates, tartaric acid, and the tartrates, increases the solubility of arsenic trioxide in water.

A solution of the acid in dilute hydrochloric acid is officinal—*Liquor arsenici hydrochloricus* (U. S., Br.), and, when made according to the directions of the Pharmacopœia, does not contain arsenic trichloride, but is simply a solution of arsenious acid in diluted hydrochloric acid.

Arsenic trioxide is less soluble in fluids containing fats or extractive or other organic matters (the various liquid articles of food), than it is in pure water.

In chemico-legal cases, in which the question of the solubility of arsenic is very likely to arise, it must not be forgotten that the quantity of arsenic trioxide which a person may unconsciously take in a given quantity of fluid is not limited, under certain circumstances, to that which the fluid is capable of *dissolving;* a much greater quantity than this may be taken while in suspension in the liquid, especially if it be mucilaginous.

Arsenic trioxide is readily decomposed by reducing agents, elementary arsenic being deposited, a decomposition which occurs when it is heated with hydrogen, carbon, potassium cyanide, etc.; and at a lower temperature by more active reducing agents. Oxydizing agents, on the other hand, such as nitric acid, the hydrates of chlorine, chromic acid, etc., convert it into arsenic pentoxide, or arsenic acid.

Its solution, acidulated with hydrochloric acid, is decomposed when boiled with metallic copper, and an alloy of copper and arsenic is de-

posited as a gray film upon the copper (see p. 127). Arsenic trioxide is largely used in the arts, in the manufacture of glass, green pigments, and vermin-poisons; in the processes of dyeing, in the preservation of anatomical preparations, and by the taxidermist. It is one of the commonest of poisons (see p. 125).

Arsenic Pentoxide.

Arsenic anhydride—As_2O_5—is obtained by heating arsenic acid to redness. It is a white, amorphous solid, which, when exposed to the air, slowly absorbs moisture. It is fusible at a dull red heat, and at a slightly higher temperature decomposes to arsenic trioxide and oxygen. It dissolves slowly in water, forming arsenic acid, AsO_4H_3.

Arsenic Acids.

These substances form a series, resembling the corresponding compounds of phosphorus. No arsenic compound corresponding to hypophosphorous acid has, however, been discovered as yet:

Arsenious acid	AsO_3H_3.
Arsenic acid	AsO_4H_3.
Pyroarsenic acid	$As_2O_5H_4$.
Metarsenic acid	AsO_3H.

Arsenious acid, AsO_3H_3.—Although this acid has not been separated, its existence in solutions of the trioxide may be presumed, especially as the solution has a faintly acid reaction. Its composition is similar to that of phosphorous acid, and, as is the case with that acid, two only of the atoms of hydrogen are replaceable. Corresponding to this acid are a number of important salts, called arsenites, which have the general composition $AsO_3HM'_2$, AsO_3HM'', $(AsO_3)_2H_4M''$.

Arsenites have also been obtained which seem to correspond to a pyroarsenious acid, $As_2O_5H_4$, and others corresponding to a metarsenious acid, AsO_2H.

Arsenic acid—Orthoarsenic acid—AsO_4H_3—is obtained by oxidizing arsenic trioxide with nitric acid, in the presence of water:

$$As_2O_3+2H_2O+2NO_3H=2AsO_4H_3+N_2O_3.$$

The oxidation may also be brought about by chlorine, aqua regia, or other oxidizing agents. A syrupy solution is thus obtained which, at 15° or below, becomes semi-solid from the formation of transparent crystals, containing one molecule of water of crystallization. These crystals, which are very deliquescent and closely resemble in appearance those of sodium sulphate, lose their water of crystallization when heated to 100°, and form a white, pasty mass composed of minute crystalline needles, which are anhydrous.

Arsenic acid is very soluble in water, the solution being strongly acid in taste and in reaction; colorless and odorless.

In the presence of nascent hydrogen, arsenic acid is decomposed with formation of water and hydrogen arsenide. It is readily converted into

the lower stage of oxidation of arsenic by the action of reducing agents. A current of sulphur dioxide passed through its solution converts it into arsenious acid. If hydrogen sulphide be passed through a solution of arsenic acid or of an arsenate, the first portions of the gas reduce the arsenical compound to arsenious acid, while sulphur separates. After this action has occurred, the arsenious acid is itself decomposed, with formation of arsenic trisulphide.

Hydrochloric acid, even when concentrated and boiling, forms with arsenic acid mere traces of arsenic trichloride.

Like phosphoric acid, arsenic acid is tribasic; and the arsenates resemble the phosphates in composition, and in many of their chemical and physical properties.

Although not as poisonous as arsenious acid (Woehler and Frerichs) *in solutions of equal strength*, it is quite as dangerous a substance, owing to its greater solubility. It is manufactured in large quantities industrially, and is used in dyeing and in the manufacture of fuchsine (*q. v.*).

Pyroarsenic acid, $As_2O_7H_4$.—The resemblance between the phosphorus acids and those of arsenic is visible in the action of heat upon arsenic acid, as well as in other properties. If arsenic acid be heated to 140°–180°, there form compact masses of hard crystals having the above composition, and formed, like pyrophosphoric acid, by the union of two molecules of the orthoacid with separation of the elements of one molecule of water. This acid is quite unstable and readily takes up the elements of water again, with regeneration of orthoarsenic acid; for this reason it is not soluble in water without decomposition. It forms salts having the same constitution as the pyrophosphates.

Metarsenic acid, AsO_3H.—If pyroarsenic (or arsenic) acid be maintained at a temperature of 200°–206° for some time, a further loss of water occurs, and an acid is formed having the composition AsO_3H, the transformation taking place rather suddenly. It appears in the form of white, pearly crystals, which dissolve readily in water, the act of solution being attended with a considerable elevation of temperature and the regeneration of arsenic acid. It is a monobasic acid.

Compounds of Arsenic and Sulphur.

Quite a number of compounds of these elements have been described, some of which are more probably mixtures than definite compounds. Three, however, are well characterized:

Arsenic disulphide.....As_2S_2.
Arsenic trisulphide.....As_2S_3.
Arsenic pentasulphide.....As_2S_5.

Arsenic disulphide—Red sulphide of arsenic—Realgar—Red orpiment—Ruby sulphur—Red sulphuret of arsenic—Sandarach—As_2S_2.—Exists in nature in the form of translucent, ruby-red crystals. It is also prepared artificially by fusing together seventy-five parts of arsenic and thirty-two parts of sulphur, or by heating a mixture of sulphur and arsenic trioxide; as so prepared it appears in brick- or ruby-red fragments, having a conchoidal fracture. It is fusible, insoluble in water, but soluble in solutions of the alkaline sulphides and in a boiling solution of potassium hydrate. It is used in the arts, in pyrotechny, and as a pigment.

Arsenic trisulphide—Orpiment—Auripigmentum—Yellow sulphide or *Sulphuret of arsenic—King's yellow*—As_2S_3.—Occurs in nature in brilliant, golden yellow flakes. Obtained artificially by passing hydrogen sulphide through a solution of arsenious acid, or by heating a mixture of arsenic and sulphur, or of arsenic trioxide and sulphur.

It is a lemon-yellow powder when obtained by precipitation, and in orange-yellow crystalline masses when prepared by sublimation.

It is almost insoluble in cold water, but sufficiently soluble in hot water to communicate to it a distinctly yellow color. By continued boiling with water it is decomposed, with formation of hydrogen sulphide and arsenious acid. The limited solution of this substance in water does not take place in the presence of a small quantity of hydrogen sulphide. It is insoluble in dilute hydrochloric acid, but very soluble in solutions of the alkaline hydrates, especially in solution of ammonium hydrate, and in solutions of the alkaline carbonates and sulphides.

Nitric acid oxidizes it quickly, forming arsenic and sulphuric acids. The same decomposition occurs with nitrohydrochloric acid, and with hydrochloric acid and potassium chlorate.

Arsenic trisulphide corresponds in constitution to the trioxide, atoms of sulphur taking the place of those of oxygen. Like that body, it may be regarded as an anhydride, although it contains no oxygen; for, notwithstanding the fact that sulpharsenious acid, AsS_3H_3, has not been separated, its existence must be regarded as possible from that of the well-characterized sulpharsenites, pyrosulpharsenites, and metasulpharsenites, similar in constitution to the salts of the corresponding oxygen acids.

Orpiment is used in the arts as a pigment, under the name of *King's yellow*, and, as such, has given rise to many cases of so called "accidental" poisoning, by being mistaken for more harmless coloring matters and introduced into articles of food with more or less innocent intent. Although the natural product is probably inert, the artificial is actively poisonous, from the presence in it of arsenic trioxide. In cases of death from arsenical poisoning, the arsenic is liable to be converted into the trisulphide, after long burial.

Arsenic pentasulphide, As_2S_5 — is said to have been obtained by fusing a mixture of the trisulphide and sulphur in proper proportions, as a yellow, fusible solid, capable of sublimation in the absence of air. The precipitate which is formed when a solution of an arsenate is treated with hydrogen sulphide is not this substance, but a mixture of the trisulphide and sulphur. Whether or no this body exists in the free state (and its existence has been called in question), there exist well-defined salts, sulpharsenates, pyrosulpharsenates, and metasulpharsenates, to which this body bears the same relation that arsenic pentoxide does to the corresponding oxygen compounds.

Compounds of Arsenic with the Elements of the Chlorine Group.

Arsenic trifluoride, AsF_3—a colorless, fuming liquid, boiling at 63°, capable of attacking glass, obtained by distilling a mixture of arsenic trioxide, fluorspar, and sulphuric acid.

Arsenic trichloride, $AsCl_3$.—Obtained by distilling a mixture of arsenic trichloride, sulphuric acid, and sodium chloride, using a well-cooled receiver.

It is a colorless liquid, boils at 134°, fumes when exposed to the air, and volatilizes readily at temperatures below its boiling-point. Its formation must be avoided in processes for the chemico-legal detection of arsenic, lest it be volatilized and lost.

It is formed by the action of hydrochloric acid, even when comparatively dilute, upon arsenic trioxide at the temperature of the water-bath; but, if potassium chlorate be added, the trioxide is oxidized to arsenic acid, and the formation of the chloride thus prevented. Arsenic trioxide, when fused with sodium nitrate, is converted into sodium arsenate, which is not volatile; if, however, small quantities of chlorides be present, arsenic trichloride is formed (see p. 129). It is highly poisonous.

Arsenic tribromide, $AsBr_3$.—Obtained by adding powdered arsenic to bromine, and distilling the product at 220°. A solid, colorless, crystalline body, fuses at 20°–25°, boils at 220°, and is decomposed on contact with water.

Arsenic triiodide, AsI_3.—Obtained by adding arsenic to a solution of iodine in carbon disulphide, or by fusing together arsenic and iodine in proper proportions. A brick-red solid, fusible and capable of volatilizing unchanged. In a large quantity of water it dissolves; with a small quantity it is decomposed, with formation of hydriodic acid, arsenic trioxide, water, and a residue of arsenic triiodide.

Arsenic triiodide, prepared by fusion, is officinal as *Arsenici iodidum*, (U. S.), and enters into the composition of the *Liq. arsenici et hydrargyri iodidi* (U. S.), or Donovan's solution.

Action of Arsenical Compounds upon the Animal Economy.

The poisonous nature of many of the arsenical compounds has been known from a remote period, and it is probable that more murders have been committed by their use than by that of all other toxic substances combined. Even at the present time—notwithstanding the fact that, suspicion once aroused, the detection of arsenic in the dead body is certain and comparatively easy—criminal arsenical poisoning is still quite common, especially in rural districts. It would seem, however, that in France, phosphorus is more frequently used; while in England, opium and its preparations are the favorite agents of the poisoner.

Of poisons used by suicides in this country, the arsenical compounds (especially Paris green, aceto-arsenite of copper) maintain their position at the head of the list. The great majority of cases of arsenical poisoning which come to our notice are suicidal; we are forced, however, by statistics and experience, to believe that this proportion would be much reduced were it not that the secrecy enshrouding homicidal poisoning is only penetrated in a small percentage of cases—not from the fault of the chemist, but from that of physicians, coroners, and other prosecuting officers.*

The poison usually enters the circulation by the alimentary canal, being taken by the mouth; but instances are not wanting in which it has

* The last conviction of the crime of murder by poison in New York City was that of Stephens, in 1858. During the following period of nearly a quarter of a century. Paris and London have witnessed many trials of cases of homicidal poisoning, while New York would seem to be either free from the crime, or a safe place for those who desire to murder in this way.

been introduced in other ways: by the skin, to which it has been applied in the form of ointment; by abraded surfaces, to which it has been applied by quacks as a "cancer cure;" by the rectum, vagina, or male urethra.

The substances taken or administered have been:

First.—Elementary arsenic, usually in the shape of fly-poison, which, however, contains arsenic trioxide as well. Elementary arsenic is not poisonous *so long as it remains such;* in contact with water, or with the saliva, however, it is converted into an oxide, which is then dissolved, and, being capable of absorption, produces the characteristic effects of the arsenical compounds.

Second.—Hydrogen arsenide, the most actively poisonous of the inorganic compounds of arsenic, has not been used by the homicide or the suicide. Several cases of accidental death from its effects have been recorded, prominent among which is that of the chemist Gehlen, who died in consequence of having inhaled a few bubbles of the gas while experimenting upon it. In other cases death has followed the inhalation of hydrogen, made from zinc, or sulphuric acid contaminated with arsenic.

Third.—Arsenic trioxide has been the substance administered in a great number of cases of homicidal poisoning, has been used to a limited extent by suicides, and has been frequently taken or administered by mistake or accident. It has been given by every channel of entrance to the circulation; in some instances concealed with great art, in others merely held in suspension by stirring in a transparent fluid given to an intoxicated person. If the poison have been given in quantity, and undissolved, it may be found in the stomach after death in the form of eight-sided crystals, more or less worn by the action of the solvents with which it has come in contact.

The lethal dose is variable, death having occurred from two and one-half grains, and recovery having followed the taking of a dose of two ounces. It is more active when taken fasting than when taken on a full stomach, in which latter case all, or nearly all, the poison is frequently expelled by vomiting, before there has been time for the absorption of more than a small quantity.

Fourth.—Potassium arsenite, the active substance in "Fowler's solution," although largely used by the laity in malarial districts as an ague-cure, has, so far as the records show, produced but one case of fatal poisoning.

Fifth.—Sodium arsenite is sometimes used to clean metal vessels, a practice whose natural results are exemplified in the death of an individual who drank beer from a pewter mug so cleaned; and in the serious illness of three hundred and forty children in an English institution, in which this material had been used for cleaning the water-boiler.

Sixth—Arsenic acid and *arsenates.*—The acid itself has, so far as we know, been directly fatal to no one. The cases of death and illness, however, which have been put to the account of the red anilin dyes, are not due to them directly, but to arsenical residues remaining in them as the result of careless processes of manufacture.

Seventh.—Sulphides of arsenic.—Poisoning by these is generally due to the use of orpiment, introduced into articles of food as a coloring matter, by a combination of fraud and stupidity, in mistake for turmeric.

Eighth.—The arsenical greens.—Scheele's green or cupric arsenite, and Schweinfurth green or cupric aceto-metarsenite (the latter commonly known in the United States as Paris green, a name applied in

Europe to one of the anilin pigments). These substances, although rarely administered with murderous intent, have been the cause of death in a great number of cases. Among suicides in the lower orders of the population in large cities, Paris green has been the favorite.

The arsenical pigments may also produce disastrous results by "accident;" by being incorporated in ornamental pieces of confectionery; by being used in the dyeing of textile fabrics, from which they may be easily rubbed off; and by being used in the manufacture of wall-paper. Many instances of chronic or subacute arsenical poisoning have resulted from inhabiting rooms hung with paper whose whites, reds, or greens were produced by arsenical pigments. From such paper the poison is disseminated in the atmosphere of the room in two ways: either as an impalpable powder, mechanically detached from the paper and floating in the air, or, as Fleck has shown, by their decomposition, and the consequent diffusion of volatile arsenical compounds in the air.

The *treatment* in acute arsenical poisoning is the same, whatever may be the form in which the poison has been taken. The first indication is the removal of any unabsorbed poison from the alimentary canal. If vomiting have not occurred from the effects of the toxic, it should be induced by the administration of zinc sulphate, or by mechanical means. The stomach-pump should not be used unless the case is seen soon after the taking of the poison. When the stomach has been emptied, the chemical antidote is to be administered, with a view to the transformation in the stomach of any remaining arsenical compound into the insoluble, and, therefor, innocuous ferrous arsenate. From recent experiences, it would seem that the preparation known as "dialyzed iron" is very efficacious; failing this, ferric hydrate must be prepared extemporaneously, as when dry or not recently prepared it has no longer the power of combining with the arsenical compound. To prepare this substance a solution of ferric sulphate, *Liq. ferri tersulphatis* (U. S.) = *Liq. ferri persulphatis* (Br.), is diluted with three volumes of water and treated with aqua ammoniæ in slight excess. The precipitate formed is collected upon a muslin filter and washed with water until the washings are nearly tasteless. The contents of the filter—*Ferri oxidum hydratum* (U. S.), *Ferri peroxidum humidum*, (Br.)—are to be administered, while still moist, in frequently repeated doses of one or two teaspoonfuls until the fæces become black or very dark in color from the presence of ferrous sulphide. This treatment applies only to those cases in which the poison has been taken by the mouth, and has for its object the removal of those portions which are not yet absorbed. The symptoms caused by the absorbed poison are to be treated as they arise.

Toxicological Analysis.

PRECAUTIONS TO BE TAKEN BY THE PHYSICIAN.—It will rarely happen that in a case of suspected homicidal poisoning by arsenic, or by other poisons, the physician in charge will be willing or competent to conduct the chemical analysis upon which probably the conviction or acquittal of the accused will mainly depend. Upon his knowledge and care, however, the success or futility of the chemist's labors depend in a great measure.

It is, as a rule, the physician who first suspects foul play; and, while it is undoubtedly his duty to avoid any public manifestation of his suspicion, it is just as certainly his duty toward his patient and toward the com-

munity to satisfy himself as to the truth or falsity of his suspicion by the application of a simple test to the excreta of the patient during life, the result of which may enable him to prevent a crime, or, failing that, take the first step toward the punishment of the criminal.

In a case in which, from the symptoms, the physician suspects poisoning by any substance, he should himself test the urine or fæces, or both, and govern his treatment and his actions toward the patient, and those surrounding the patient, by the results of his examination. Should the case terminate fatally, he should at once communicate his suspicions to the prosecuting officer, and require a post-mortem investigation, which should, if at all possible, be conducted in the presence of the chemist who is to conduct the analysis; for, be the physician as skilled as he may be, there are odors and appearances, observable in many cases at the opening of the body, full of meaning to the toxicological chemist, which are ephemeral, and whose bearing upon the case is not readily recognized by those not thoroughly experienced.

Cases frequently arise in which it is impossible to bring the chemist upon the ground in time for the autopsy; in such cases the physician should remember that that portion of the poison remaining in the alimentary tract (we are speaking of true poisons) is but the residue of the dose in excess of that which has been necessary to produce death; and, if the processes of elimination have been active, there may remain no trace of the poison in the alimentary canal, while it still may be detectable in deeper-seated organs. Moreover, the finding of poison in the stomach alone would not, at the present time, be sufficient to procure conviction of the criminal, who might raise the very plausible question as to whether the poison was not injected by some malicious person into that viscus after death.

For these reasons it is not sufficient to send the stomach alone for analysis; the chemist should also receive the entire intestinal canal, at least one-half the liver, the spleen, one or both kidneys, a piece of muscular tissue, the brain, and any urine that may remain in the bladder. The intestinal canal should be removed and sent to the chemist *without having been opened*, and with ligatures enclosing the contents at the two ends of the stomach and at the lower end of the intestine. The brain and alimentary canal are to be placed in separate jars, and the other viscera in another jar together; the urine in a vial by itself. All of these vessels are to be new and clean, and are to be closed by new corks, or by glass stoppers, or covers (not zinc screw-caps), which are then coated with paraffine (not sealing-wax), and so fastened with strings and seals that it is impossible to open the vessels without cutting the strings or breaking the seals. If the physician fail to observe these precautions, he has probably made the breach in the evidence through which the criminal will escape, and has at the outset defeated the aim of the analysis.

Toxicological analysis.—Since the earlier days of toxicological chemistry many processes for the detection of arsenic have been suggested, varying greatly as to the facility of their application and the reliability of the results obtained.

Of these there is one which, although well adapted to the use of physicians during the life of the patient, is of little value from a chemico-legal point of view; we refer to Reinsch's test.

The advantages of this method are that it may be applied to solutions containing organic matter, the urine for instance; it is easily conducted, and its positive results are not misleading, *if the test be carried to completion.* It is, therefor, the test which we should recommend physicians

to apply to the urine, in cases which they suspect are due to arsenical poisoning; but at the same time it is one whose application to any solid or fluid, *after death*, we should disapprove of strongly, unless complete evidence of the presence of the poison had already been obtained by the use of other tests. By its use copper is introduced into the substances examined, which may seriously interfere with subsequent steps in the analysis, by rendering impossible a distinction between poisoning by arsenious anhydride and that by Paris green—a distinction which may become of vital importance if the defence claim the case to be one of suicide. Other disadvantages of Reinsch's test are that it is not as delicate as Marsh's test; that by it arsenic in its higher state of oxidation is not detected; the difficulty of obtaining copper free from arsenic; and that its results are interfered with by the presence in the mixture tested of oxidizing agents.

Reinsch's test consists in acidulating the suspected fluid (urine) with one-sixth its bulk of pure hydrochloric acid, immersing in the liquid a strip of pure electrotype copper, and boiling. If arsenic be present, a gray or bluish deposit will form upon the copper; but, as such a deposit is produced by other substances (bismuth, antimony, mercury) as well as arsenic, the mere formation of this stain is not evidence of the presence of an arsenical compound. To complete the test the copper is removed, washed, and dried between folds of filter paper, without removing the deposit. The copper, with its adhering deposit, is then rolled into a little cylinder, which is introduced into a piece of Bohemian tubing, about one-fourth of an inch in diameter and six inches long. The tube is then held at an angle of about 45°, the copper coil being about an inch and a half from the lower end, and heated at the point where the copper is. If the deposit be due to arsenic, a sublimate, consisting of octahedral crystals of arsenic trioxide, will form at some point in the upper, cool portion of the tube.

Three precautions must be observed by the physician in using this test: 1. The freedom of the hydrochloric acid and copper from arsenic must be demonstrated by a blank testing. 2. No stain upon the copper is evidence of the presence of arsenic, unless it yield crystals of the trioxide as described. 3. It should never be used after the death of the patient, especially if there be any reason to believe that the case will be the subject of legal proceedings.

In a case of supposed homicidal poisoning the analyst must not confine his attention to any one poison, however directly the circumstances of the case may point to the use of this or that toxic. He must so conduct the analysis as to be enabled to predicate the absence or presence of each of the more usually employed poisons. For this reason a systematic course of analysis must be followed, in which the search for mineral poisons, phosphorus excepted, follows that of those of an organic nature. This arrangement is chosen, firstly, because the volatile and some of the alkaloidal poisons, being subject to decomposition in contact with putrefying organic material, must be sought for at the earliest possible moment; and secondly, because, in searching for mineral poisons, it is necessary to destroy all organic matter, the presence of which would render the tests applied uncertain, and in many instances delusive.

The best method of accomplishing this destruction of organic matter is that devised by Frezenius and von Babo. It consists in oxidizing the animal or vegetable substances by a mixture of hydrochloric acid and potassium chlorate. The material to be examined, divided into small

pieces if solid, is rendered fluid by the addition of water, and, after the addition of about 200 c.c. of hydrochloric acid, and four to five grams of potassium chlorate, is heated over the water-bath, small quantities of chlorate being added from time to time until the mass has a uniform light yellow color. If now it smell strongly of chlorine, it is warmed, and treated with a current of carbon dioxide until the chlorine odor has disappeared, when it is allowed to cool, is filtered, and the residue washed with hot water. The clear filtrate and washings, if strongly acid, are *partially* neutralized by the addition of sodium carbonate, and treated with a current of washed hydrogen sulphide, the gas being passed through the warmed liquid until, after shaking, it retains a strong odor of sulphuretted hydrogen. The vessel is then corked and set aside until the following day, when the same treatment is repeated, as again on a third day, a long contact with an excess of hydrogen sulphide effecting a more complete separation of the metallic sulphides than a treatment with a large volume of the gas during a shorter period. The precipitate formed is now collected upon a filter, and washed with water containing a small quantity of hydrogen sulphide, until the washings do not give the faintest cloudiness when boiled, acidulated with nitric acid, and tested for chlorides by the addition of silver nitrate solution.

The precipitate is then treated with solution of ammonium sulphydrate, which effects a partial separation of the poisonous metals, some being dissolved and others remaining; arsenic trisulphide will pass into the solution. This is now evaporated over the water-bath to dryness, the residue moistened with strong nitric acid and again dried over the water-bath, the treatment with nitric acid being repeated two or three times. To the residue sodium carbonate and sodium nitrate are added, and the whole heated to fusion until colorless. It is then allowed to cool, and decomposed by the addition of strong sulphuric acid and gradual heating until all nitric acid is expelled, and until copious white fumes are given off. The residue is finally dissolved in water, and if there be any cloudiness in the solution (see p. 132), it is filtered and tested for arsenic by one of the following methods:

Of all the tests hitherto devised for the detection of arsenic, the most delicate and the most certain is that originally suggested by James Marsh, in 1836, and subsequently so modified by Berzelius, Otto, and others, that but little of the original method remains beyond the principles upon which it is based (see p. 117). The apparatus consists of a generating flask having a capacity of about 75 c.c., fitted with a cork through which pass a funnel-tube, drawn out and turned up at the lower end, and a tube bent to a right angle and carrying a bulb upon its horizontal limb. This tube communicates with a drying-tube, filled with fragments of calcium chloride enclosed between cotton plugs, and this in turn with a piece of Bohemian tubing, about an eighth of an inch in diameter and about two feet long, whose middle third is coiled in a spiral; finally, this tube is connected with a right-angle tube, whose lower extremity dips into a solution of silver nitrate.

To apply the test, the generating flask is charged with pure zinc, which is moistened with water containing a few drops of a solution of platinum chloride; the solution is allowed to remain upon the zinc about ten minutes, and is then washed off. The apparatus is mounted in such a way that all its joints are gas-tight, and sulphuric acid, diluted with a little more than its bulk of water and cooled, is poured into the funnel-tube. After the generation of hydrogen has continued for about twenty

minutes, the coiled portion of the Bohemian tube is heated to redness, and the heating and evolution of hydrogen continued for a full half-hour. If at the end of this time the faintest deposit have formed in the cool portion of the tube, beyond the coil, the chemicals are to be rejected as impure, and the testing is to be repeated with others. If no deposit have formed, the suspected liquid, diluted *if necessary* with water, is slowly introduced through the funnel-tube in such a way that *no air* is carried down with it, that the generating flask does not become hot, and that the introduction of the entire quantity (which should not measure more than two or three fluid ounces) shall require from an hour to an hour and a half. If the proper precautions have been observed, and if the matters tested contained arsenic, a hair-brown or steel-gray deposit will have formed in the tube, beyond the coil.

As Marsh's test is usually applied, this stain may be produced by antimony as well as by arsenic; but if the method indicated above have been followed, antimony, if present, will have been separated at an earlier stage of the process (see page 132).

Some toxicologists direct that the final exit of the gas from a Marsh apparatus be from a drawn-out end of the tube, pointing upward, and that it shall be there ignited. If, under these conditions, the heating of the coil be discontinued, in the presence of arsenic a white, crystalline deposit of arsenic trioxide may be collected upon a glass surface held above the flame, or a brown or black deposit of elementary arsenic upon a cold, white, porcelain surface held in the flame. But this method—the original form of Marsh's test—is attended with a considerable loss of arsenic, and we therefor consider it preferable to collect any arsenic which may escape deposition in the tube in a solution of silver nitrate. The presence of arsenic in the silver solution may be subsequently detected by cautiously floating a small quantity of dilute ammonium hydrate solution upon the surface of the liquid, when a yellow cloudiness is observed at the line of contact.

Owing to the difficulty formerly experienced in obtaining zinc free from arsenic, it was suggested that nascent hydrogen be obtained by the decomposition of acidulated water by the battery. This modification of the Marsh process is usually designated as Bloxam's test, as its use was recommended by that chemist in 1860; a similar apparatus was, however, suggested by Morton previous to 1847.

If a determination of the quantity of arsenic present be required, the sulphuric acid solution obtained as directed on page 129 is not introduced directly into the Marsh apparatus, but is treated with sulphur dioxide, and then, after boiling until the excess of sulphur dioxide is driven off, with hydrogen sulphide. Any arsenic present is thus precipitated as the sulphide, in which form it is weighed, with the precautions indicated in the works on analytical chemistry. The estimation of arsenic as uranium or magnesium pyroarsenate, although excellent for technical purposes, is not available for the small quantities which the toxicologist has usually to deal with. The method by weighing the deposit formed in the Marsh test, recently suggested by Gautier, is not reliable.

Another test is that suggested by Frezenius and von Babo. It consists in mixing the precipitate of sulphide, obtained as above, with a mixture of potassium cyanide and sodium carbonate, and heating in a tube through which passes a slow current of carbon dioxide. If arsenic be present it will appear in the cool part of the tube as a steel-gray deposit.

To distinguish between an arsenite and an arsenate in solution, ad-

vantage is taken of the colors of the two salts of silver. To the *faintly* acid solution to be tested, neutral solution of silver nitrate is added, and the mixture then rendered neutral by blowing upon it over the glass stopper of a bottle moistened with ammonium hydrate solution. If an arsenite be present, the bright yellow silver arsenite is formed; and if an arsenate, the brick-red silver arsenate.

ANTIMONY.

Stibium.....Sb.....122

First described, about the middle of the fifteenth century, by Basil Valentine. Occurs in nature, in its elementary form, in small quantity. Its chief ore, which was known to the ancients as στίμμι, στίβι and *stibium*, is the trisulphide (*q. v.*).

The element is obtained by roasting the sulphide, which is known in commerce as *black antimony*, or *crude antimony*, and reducing the oxide so obtained by heating it with charcoal. As the commercial product, known as *regulus of antimony*, is always contaminated with other substances, notably with arsenic, it is necessary to purify it when it is to be used for medicinal or chemical purposes. This purification is effected by fusing a mixture of sixteen parts of commercial antimony, one part of the native trisulphide of antimony, and two parts of dry sodium carbonate. After cooling, the antimony is removed, powdered, and again fused with one and one-half part of sodium carbonate and one per cent. of ferrous sulphide; finally, the antimony is again separated, powdered, and fused a third time with one part of sodium carbonate and a few fragments of sodium nitrate. Each fusion is maintained for an hour.

Antimony is a bluish gray solid, having a brilliant metallic lustre, readily crystallizable by fusion and cooling; very brittle and easily pulverized. Sp. gr. 6.715. It is tasteless and odorless, melts at 450°, volatilizes at a bright red heat, and may be distilled in an atmosphere of hydrogen.

In its chemical properties and its compounds, antimony resembles arsenic; it is not, however, as readily oxidized as that element, being unaltered by exposure to air, dry or moist, at ordinary temperatures. When sufficiently heated in air it burns, with formation of the trioxide, as a white, crystalline sublimate, formerly known as *argentine flowers of antimony*. If melted antimony be dropped from a height, the small globules, exposing a large surface are rapidly oxidized, and in their passage through the air are followed by a white train of the trioxide. Antimony also unites directly with chlorine, bromine, iodine, sulphur, and with many metallic elements. Like arsenic, it unites indirectly with hydrogen.

Cold, dilute sulphuric acid is without action on antimony; the hot concentrated acid converts it into antimonyl sulphate, while sulphur dioxide is given off. When very finely divided, antimony is dissolved by hydrochloric acid under the influence of heat. Nitric acid oxidizes it readily with formation of antimonic acid, or of the intermediate oxide, Sb_2O_4. It is readily dissolved by aqua regia, with which it forms either the trichloride, $SbCl_3$, or the pentachloride, $SbCl_5$. It is not dissolved by solutions of the alkaline hydrates.

The element itself does not form salts with the oxacids. There are, however, compounds which are formed by the substitution of the group $(SbO)'$, an univalent radical, for the basic hydrogen of those acids. Similar compounds of vanadium and of arsenic are also known (see Tartar Emetic, p. 405).

Antimony is also capable of uniting with many metals to form alloys, some of which are definite, crystalline compounds.

Antimony is largely used in the arts, chiefly in the form of alloys, to which it communicates hardness and the property of expanding at the moment of solidification. Its principal use is as a constituent of type-metal; it also enters into the composition of "Britannia metal," "Queen's metal," and of the various anti-friction alloys used for the bearings of machinery. In a finely divided state it is applied to papier maché and plaster ornaments, to give them the appearance of steel. It is not used in medicine in its elementary form.

Hydrogen Antimonide.

Antimoniuretted hydrogen — Stibamine — Stibonia — SbH_3. — Does not exist in nature, and has not as yet been obtained in a state of purity, being always mixed with a large quantity of hydrogen. Its composition, SbH_3, corresponding to that of the hydrogen compounds of the other elements of this group, has been established beyond a doubt by the study of its products of substitution.

It is a gaseous substance, formed from reducible compounds of antimony, under the same conditions which govern the formation of hydrogen arsenide. It is also subject to decompositions, similar to those of the arsenical compound. It differs from hydrogen arsenide in being by no means as poisonous, and in its action upon solutions of silver nitrate. Hydrogen arsenide, when passed through a solution of the silver salt, is decomposed according to the equation—

$$6NO_3Ag + AsH_3 + 3H_2O = 6NO_3H + AsO_3H_3 + 3Ag_2,$$

elementary silver being separated as a black powder, while arsenious acid remains in the solution, from which the yellow silver arsenite may be precipitated by cautiously floating dilute ammonium hydrate upon the surface of the clear liquid.

In the case of hydrogen antimonide, a black deposit is also formed, but in this instance it is not elementary silver, but silver antimonide:

$$3NO_3Ag + SbH_3 = 3NO_3H + SbAg_3.$$

Distinction between Arsenic and Antimony by Marsh's Test.

If the analysis have been conducted in the manner indicated upon p. 128, any antimony present is separated during the fusion with sodium nitrate and carbonate, and the subsequent solution and filtration, as an insoluble white powder, from which the element may be obtained by fusion with potassium cyanide, and its nature determined by solution in

aqua regia, which solution is then tested for antimony (see p. 138). If, however, Marsh's test be applied without the previous steps in the process, the stain of arsenic may be distinguished from that of antimony by the following differences:

The Arsenical Stain.	*The Antimonial Stain.*
First.—Is farther removed from the heated portion of the tube, and, if small in quantity, is double—the first hair-brown, the second steel-gray.	*First.*—Is quite near the heated portion of the tube.
Second.—Volatilizes readily when heated in an atmosphere of hydrogen, being deposited farther along in the tube; the escaping gas has the odor of garlic.	*Second.*—Requires a much higher temperature for its volatilization; fuses before volatilizing. Escaping gas has no alliaceous odor.
Third.—When cautiously heated in a current of oxygen, brilliant white octahedral crystals of arsenic trioxide are deposited farther along in the tube.	*Third.*—No crystals formed by heating in oxygen.
Fourth.—Instantly soluble in solution of sodium hypochlorite.	*Fourth.*—Insoluble in solution of sodium hypochlorite.
Fifth.—Slowly dissolved by solution of ammonium sulphydrate; more rapidly when warmed.	*Fifth.*—Dissolves quickly in solution of ammonium sulphydrate.
Sixth.—The solution obtained in 5° leaves, on evaporation over the water-bath, a bright yellow residue.	*Sixth.*—The solution obtained in 5° leaves, on evaporation over the water-bath, an orange-red residue.
Seventh.—The residue obtained in 6° is soluble in aqua ammoniæ, but insoluble in hydrochloric acid.	*Seventh.*—The residue obtained in 6° is insoluble in aqua ammoniæ, but soluble in hydrochloric acid.
Eighth.—Is soluble in warm nitric acid; the solution on evaporation yields a white residue, which turns brick-red when moistened with silver nitrate solution.	*Eighth.*—Is soluble in warm nitric acid; the solution on evaporation yields a white residue, which is not colored when moistened with silver nitrate solution.
Ninth.—Is not dissolved by a solution of stannous chloride.	*Ninth.*—Dissolves slowly in solution of stannous chloride.

When, from the methods followed, it is doubtful whether the stain be antimonial or arsenical, it is well to use a number of small coils of heated tubing (see p. 129), through which the gas is made to pass in succession, rather than to attempt the collection of stains by the introduction of porcelain surfaces into the flame of the jet ignited as it issues from the end of the tube, as by the latter method of manipulation much of the antimony is lost. In conducting the Marsh test for antimony the precautions mentioned on p. 130 are to be observed.

Compounds of Antimony and Oxygen.

Three compounds of these elements are known:

Antimony trioxide.....Sb_2O_3.
Antimony pentoxide .....Sb_2O_5.
Intermediate oxide.....Sb_3O_4.

Antimony trioxide—Antimonious anhydride—Oxide of antimony—Antimonii oxidum(U. S., Br.)—Sb_2O_3—exists in nature, and is worked

as an ore of antimony in Algeria. It is, however, generally prepared artificially for use in the arts and medicine, by decomposing the oxychloride (*q. v.*). This decomposition may be effected in a variety of ways. The best method of obtaining the pure oxide consists in simply heating the oxychloride strongly in a crucible, when it is decomposed into trioxide and trichloride, the latter being volatilized. The United States Pharmacopœia process consists in first obtaining the oxychloride, which is then decomposed by dilute ammonium hydrate solution, and washing to separate the ammonium chloride formed. The British Pharmacopœia process is similar, but the decomposition is effected by a solution of sodium carbonate, instead of by ammonium hydrate. Antimony trioxide is also formed by heating antimony in a current of air, in the form of brilliant prismatic crystals, known formerly as Flores antimonii argentei, or Nix stibii.

As prepared by the wet process, it is an amorphous, tasteless, and odorless powder, white at ordinary temperatures, but turning temporarily yellow when heated. It fuses readily, and, if protected from the oxygen of the air, volatilizes and condenses in the form of prismatic crystals. If strongly heated in contact with air, it burns like tinder, and is converted into the intermediate oxide, Sb_2O_4. It is insoluble in water.

It is readily reduced, with separation of elementary antimony, when heated with carbon or in an atmosphere of hydrogen. It is also readily oxidized, as when brought in contact with nitric acid, or with solution of potassium permanganate. It dissolves in hydrochloric acid, with formation of the trichloride; in Nordhausen sulphuric acid, from which solution there separate brilliant crystalline plates, having the composition $S_2O_7(SbO)_2$. It dissolves readily in solution of tartaric acid or of hydropotassic tartrate (see Tartar Emetic). By boiling solutions of the alkaline hydrates it is gradually converted into antimonic acid.

James' Powder, *Pulvis antimonialis* (Br.) is a mixture of antimony trioxide and tricalcic phosphate.

Antimony pentoxide—Antimonic anhydride—Sb_2O_5—is obtained by heating metantimonic acid to dull redness. It is an amorphous, tasteless, and odorless solid, pale lemon-yellow when cool, and becoming temporarily darkened when heated. When heated to redness it gives off oxygen, and the intermediate oxide remains. It is very sparingly soluble in water and in acids.

Intermediate oxide, Sb_2O_4—occurs in nature. It is formed when the oxides or hydrates of antimony are strongly heated, or when the lower stages of oxidation or the sulphides are oxidized by nitric acid, or by fusion with sodium nitrate. It is insoluble in water, but decomposed by hydrochloric acid, hydropotassic tartrate, and potash.

The constitution of this compound is still undetermined. It is regarded as the antimonic salt of metantimonic acid, $SbO_3(SbO)'$, or as the anhydride corresponding to an acid having the composition $Sb_2O_5H_2$. The latter view is probably the correct one, as by treatment with potash it yields a compound having the composition $Sb_2O_5K_2$, which, by decomposition with an equivalent quantity of sulphuric acid, yields the acid $Sb_2O_5H_2$. Moreover, there exists in nature a mineral (romeine) which is the calcium salt Sb_2O_5Ca.

Antimony Acids.

The normal antimonous acid, SbO_3H_3, corresponding to phosphorous acid, is not known; but the series of antimonic acids is complete, either in the form of salts or in that of the free acid:

Orthoantimonic acid.....SbO_4H_3.
Pyroantimonic acid.....$Sb_2O_7H_4$.
Metantimonic acid .....SbO_3H.

Besides these there also exists, in the shape of its sodium salt, a derivative of the lacking antimonous acid:

Metantimonous acid.....SbO_2H.

But little practical interest attaches to these acids, or to their salts. The compound sometimes used in medicine under the name *washed diaphoretic antimony* is potassium metantimonate, united with an excess of antimony pentoxide, $2SbO_3K$, Sb_2O_5.

The hydropotassic pyroantimonate, $Sb_2O_7K_2H_2$, 6Aq, is a valuable reagent for sodium, with which it forms the insoluble sodium salt. The reagent is obtained by calcining a mixture of one part of antimony with four parts of potassium nitrate, fusing the product with its own weight of potassium carbonate, and dissolving the resulting white mass in water as it is required for use.

Chlorides of Antimony.

Two chlorides and several oxychlorides are known:

Antimony trichloride—Protochloride of antimony—Butter of antimony—$SbCl_3$—is obtained by passing dry chlorine over an excess of antimony or of antimony trisulphide, or by dissolving the trisulphide in hydrochloric acid, or by distilling together mixtures, either of antimony trisulphide and mercuric chloride, or of antimony and mercuric chloride, or of antimonyl pyrosulphate and sodium chloride.

At low temperatures it is a solid, crystalline body; at the ordinary temperature, a yellow, semi-solid mass, resembling butter; at 73.2° it melts to a yellow, oily liquid, which boils at 223°.

When obtained by solution of the trisulphide in hydrochloric acid of the usual strength, it forms a solution with the water, which, concentrated to sp. gr. 1.47, is the *Liq. antimonii chloridi* (U. S., Br.), used as an escharotic.

The trichloride attracts moisture from the air and is soluble in a very small quantity of water. Upon the addition of a larger quantity of water, however, the chloride is decomposed, and a white powder is formed, which was formerly known as *powder of algaroth*, and which is now prepared as a step in the manufacture of the trioxide and of tartar emetic. The composition of this substance varies according as hot or cold water is used; if the latter, the decomposition is—

$$SbCl_3+H_2O=2HCl+SbOCl;$$

but if the water be boiling—

$$4SbCl_3+5H_2O=10HCl+Sb_4O_5Cl_2.$$

In water which contains at least fifteen per cent. of hydrochloric acid, antimony trichloride dissolves without the formation of a precipitate.

Several cases of poisoning by butter of antimony, or by the *Liq. antimonii chloridi*, are upon record, the substance acting both locally as a corrosive and as a true poison.

It is used in the bronzing of gun-barrels.

Antimony pentachloride, $SbCl_5$—is formed by the action of chlorine in excess upon antimony or antimony trichloride, and distillation in a current of chlorine.

It is a fuming, colorless liquid, which solidifies at —20°, but does not melt again until the temperature reaches —6°. It absorbs moisture from the air. With a very small quantity of water, and by evaporation over sulphuric acid, it forms a hydrate having the composition $SbCl_5$, $4H_2O$, which appears in the form of transparent, deliquescent crystals. With more water a crystalline oxychloride, $SbOCl_3$, is formed; and with a still larger quantity, a white precipitate of orthoantimonic acid, SbO_4H_3, is formed. It is capable of uniting with other chlorides to form double compounds, such as $SbCl_3$, PCl_5.

With iodine, bromine, and fluorine, antimony forms compounds similar in composition to the trichloride. The triiodide, SbI_3, has been used in medicine. In its preparation the constituents must be brought together gradually to avoid explosions.

Sulphides and Oxysulphides of Antimony.

Two sulphides of antimony and a number of ill-defined oxysulphides are known.

Antimony trisulphide—Black antimony—Sulphuret of antimony—Antimonii sulphuretum (U. S.) SbS_3.—Occurs in nature, and is the chief ore of antimony; it is also formed artificially when an excess of hydrogen sulphide is passed through a solution of tartar emetic. The native sulphide is in the form of steel-gray, crystalline masses; the artificial product appears as an orange-red or brownish red, amorphous powder. It is met with in commerce, under the name "crude antimony," in conical loaves, obtained by simple fusion of the native sulphide to free it from gangue.

It is soft, readily powdered, quite fusible, and has a brilliant metallic lustre. When heated in contact with air it is decomposed, sulphur dioxide is given off, and there remains a brown, vitreous, more or less transparent mass, composed of varying proportions of oxide and oxysulphides, known as *crocus*, or *liver*, or *glass of antimony*.

An oxysulphide of a fine red color, used as a pigment under the name *antimony cinnabar* or *antimony vermilion*, is obtained by the action, under the influence of heat, of a solution of sodium hyposulphite upon a solution of antimony trichloride, or of tartar emetic. It has the composition $Sb_6S_6O_3$.

Antimony trisulphide is an anhydride, corresponding to which are salts known as sulphantimonites, having the general formula $SbS_3M'_3H$. If an excess of the trisulphide be boiled with a solution of hydrate of

potassium, or of sodium, a solution is obtained containing an alkaline sulphantimonite and an excess of antimony trisulphide. If this solution be filtered and decomposed while still hot, an orange-yellow precipitate is obtained, which is the *antimonium sulphuretum* (U. S., Br.), and consists of a mixture, in varying proportions, of the trisulphide and the trioxide. If, however, the solution be set aside and allowed to cool, a brown, voluminous, amorphous precipitate separates, which consists of antimony trisulphide, antimony trioxide, potassium or sodium sulphide, and alkaline sulphantimonite in varying proportions, and which is known as *Kermes' mineral, antimonii oxysulphuretum* (U. S.). If now the solution from which the kermes has separated, and which still contains an alkaline sulphantimonite, be decomposed with sulphuric acid, a reddish yellow substance, known as *golden sulphuret of antimony*, and which is a mixture of tri- and pentasulphides, separates.

The precipitate obtained when hydrogen sulphide is passed through an acid solution of an antimonial compound is, according to circumstances, the trisulphide or the pentasulphide, mixed with varying quantities of free sulphur.

By the action of hydrochloric acid upon the trisulphide, hydrogen sulphide is liberated; this method of obtaining that gas for toxicological analysis, formerly resorted to, is not to be recommended. In such analyses the use of red india-rubber tubing is to be avoided, as it owes its color to a sulphide of antimony.

Antimony pentasulphide—Antimonic sulphide—Sb_2S_5—is obtained by decomposing an alkaline sulphantimonate by an acid. It is a dark orange-red, amorphous powder, readily soluble in solutions of the alkalies and alkaline sulphides, the solutions containing well-characterized salts, called sulphantimonates. One of these, sodium sulphantimonate, $SbS_4Na_3 + 9\,Aq$, known as *Schlippe's salt*, forms large, yellow crystals, soluble in water, and was formerly used in medicine.

Antimonial Poisoning.

The compounds of antimony, when taken internally, are poisonous, and act with greater or less energy as they are more or less soluble. Their poisonous nature was early recognized, and utilized to such an extent that in 1566 the French Parliament found it necessary to prohibit their use in medicine—a prohibition which was not removed until a century later.

The compound which is now the most frequent cause of antimonial poisoning is tartar emetic (see p. 405), which has proved fatal in a dose of one and one-half grain, although recovery has followed the ingestion of doses as large as half an ounce in several instances. Indeed, when large doses are taken, the chances of recovery seem to be better than after small doses, probably owing to the fact that in the former instance the poison is more quickly and more completely discharged by vomiting. When administered with murderous intent, antimonials are sometimes given in small and often repeated doses, the victim finally dying of exhaustion. When the existence of such a case is suspected, the urine should be examined.

The treatment in acute antimonial poisoning should consist, first, in inducing vomiting, if it have not already occurred, by the administration of hot water; should this fail to act, the contents of the stomach are to be removed by the stomach-pump. When this has been done, tannin in

some form, decoction of oak-bark, cinchona, nutgalls, strong tea, should be given, with a view to the conversion of any remaining poison into an insoluble compound.

The presence of antimony in the viscera is best detected by Marsh's test (see p. 132).

It must not be forgotten that antimony is very liable to contamination with arsenic, which, from defective manipulations, may find its way into the medicinal antimonials.

Analytical Reactions.

Besides the reactions of Marsh's test, the presence of antimony may be detected by the following: 1st, the formation of an orange-red precipitate when hydrogen sulphide is passed through an acid solution, the precipitate being soluble in ammonium sulphydrate and in hot hydrochloric acid; 2d, the formation of a bluish, metallic deposit upon copper immersed in a boiling solution, acidulated with hydrochloric acid—the stain, when heated in a tube open at both ends, yielding an *amorphous* white sublimate (Reinsh's test).

The determination of the quantity of antimony is difficult and requires great care; it should be converted into the oxide, Sb_2O_4, and weighed as such. Processes based upon the formation and weighing of the sulphide are apt to lead to fallacious results.

IV. BORON GROUP.

BORON.

B.....11

This element forms a group by itself, none other being known which resembles it in its chemical properties. It is trivalent in all of its compounds. It forms but one oxide, which is the anhydride of a tribasic acid. It forms no compound with hydrogen.

Boron does not exist as such in nature, but occurs in combination as boracic acid and the borates of calcium, magnesium, and sodium. It was isolated almost simultaneously by Davy, Gay-Lussac, and Thenard. It may be obtained in two allotropic forms—amorphous and crystalline.

Amorphous boron is obtained by the decomposition of its oxide by metallic sodium or potassium. It is a greenish brown powder; sparingly soluble in water, infusible; it unites directly with chlorine, bromine, oxygen, sulphur, and nitrogen.

Crystallized boron is formed when the oxide, chloride, or fluoride is reduced by aluminium; or when the amorphous variety is heated with aluminium to a high temperature, without contact of air. The product varies in color from a deep garnet red to a faint, almost colorless, yellow. The crystals are quadratic prisms, more or less transparent as they are lighter or darker in color; very hard and capable of refracting light strongly; sp. gr., 2.68. When strongly heated in oxygen, it first swells up, and finally burns at a high temperature. It generally contains small quantities of carbon and aluminium. Like amorphous boron, it burns readily in an atmosphere of chlorine. It also has a marked tendency to combine with nitrogen, being capable, at elevated temperatures, of decomposing ammonia, from which it removes the nitrogen, to form the nitride, BN, while hydrogen is liberated. It is not dissolved by any acid. It forms an alloy, or compound, with platinum, which is much more fusible than is that metal.

Boron Trioxide.

Boric anhydride—Boracic anhydride—B_2O_3.—This, the only compound of boron with oxygen, is obtained by heating boric acid to redness in a platinum vessel until all water is driven off. The oxide remains on cooling as a transparent, glass-like mass, which is used to a limited extent in blowpipe analysis.

Boric Acids.

Quite a number of acids of boron have been described, either free or as salts, all of which are hydrates of the trioxide, and all derivable from the tribasic or orthoboric acid, by loss of the elements of water. Of these the most important are ortho-, meta-, and tetraboric, or pyroboric, acids.

Orthoboric acid—Boracic acid—Boric acid—BO_3H_3—exists in nature in volcanic regions, notably in Tuscany. In this region, formerly the main source of supply of boracic acid and of borax, jets of steam, known as *suffioni*, escape through fissures in the earth on the hillsides. Over these are built a series of shallow basins, through which the vapors are made to pass, and from one to another of which water passes slowly by gravity, and in its course becomes charged with boracic acid, which is then converted into borax.

To obtain the acid, a boiling, concentrated solution of borax is slowly decomposed with an excess of sulphuric acid; on cooling the acid crystallizes out.

Orthoboric acid is in the form of brilliant, crystalline plates, unctuous to the touch; odorless; slightly bitter; soluble in twenty-five parts of water at 10°; soluble in alcohol, the alcoholic solution burning with a green flame. If an aqueous solution of boric acid be distilled, a portion of the acid is carried over with the aqueous vapors. Its solution exhibits an acid reaction with litmus paper, yet it turns turmeric paper brown, a change of color produced by the alkalies.

If orthoboric acid be heated for some time at 80°, it loses the elements of a molecule of water, and is converted into *metaboric acid*, BO_2H:

$$BO_3H_3 = H_2O + BO_2H.$$

If, however, it be heated to about 100° for about eight days, four molecules unite with loss of five molecules of water:

$$4BO_3H_3 = 5H_2O + B_4O_7H_2.$$

Tetraboric acid or *Pyroboric acid*, $B_4O_7H_2$—is a substance of little interest in itself, but whose sodium salt is the most important compound of boron. Another tetraboric acid, $B_4O_9H_6$, has also been described.

Compounds of Boron with Elements of the Chlorine Group.

The fluoride, bromide, and chloride have been described.

Boron fluoride, BF_3—is prepared by heating together boron trioxide, fluor-spar, and sulphuric acid. It is a colorless gas; fuming when exposed to the air; very soluble in water, with which it enters into combination, a part of the boron separating as boron trioxide, while an acid liquid remains, which contains *hydrofluoboric acid*, BF_4H. The fluoride is not decomposed at a red heat, but is by the alkaline metals in excess, with formation of an alkaline fluoride and elementary boron. It carbonizes organic matter, as does sulphuric acid.

Boron chloride, BCl_3—is obtained by heating dry amorphous boron in a current of chlorine, and passing the vapors into a well-cooled receiver. It is a colorless, mobile liquid; boils at 17°; sp. gr. 1.35. It is capable of uniting with ammonia to form a crystalline compound. It is completely decomposed by water, with formation of orthoboric and hydrochloric acids.

Boron bromide, BBr_3.—Formed by the action of vapor of bromine upon a mixture of boron trioxide and charcoal heated to redness. A thick, colorless liquid; boils at 90°; sp. gr. 2.69.

V. CARBON GROUP.

CARBON	C	12
SILICON	Si	28

The two elements composing this group are of great interest, and are closely related to each other by resemblances in their chemical and physical properties. They are both quadrivalent, and form hydrogen compounds in which one atom of carbon or silicon is combined with four atoms of hydrogen. The saturated oxide of each is the anhydride of a dibasic acid. They are both solid and combustible, and each occurs in three distinct allotropic conditions, one amorphous, one graphitoid, and one crystalline. The resemblances existing between their compounds are close, so far as they go. But the compounds of silicon with which we are acquainted are by no means as numerous as those of carbon, although the recent researches of Friedel would indicate that, in this respect also, the relationship between the two elements will be found to be close.

In the following table the analogies between some of the compounds of the two elements are shown:

CH_4—CO—CO_2—CO_3H_2—CCl_4—$CHCl_3$—CHI_3—C_2Cl_6—CS_2.
SiH_4— SiO_2—SiO_3H_2—$SiCl_4$—$SiHCl_3$—$SiHI_3$—Si_2Cl_6—SiS_2.

CARBON.

C.....12

An element known from remote antiquity in all its three allotropic forms, whose chemical identity and elementary nature were, however, first recognized by Lavoisier. It occurs in nature in all of its elementary forms, and in combination in the three kingdoms of nature, it being the element especially characteristic of such substances as exist only in animal and vegetable bodies.

Its three allotropic forms differ from each other widely in appearance and in other physical properties; they occur in nature as: 1st, diamond; 2d, graphite; 3d, coal.

Diamond.—Occurs in nature in octahedral crystals, in India, Brazil, Australia, and South Africa. It has also been found in North Carolina and in Georgia, in alluvial sand, clay, sandstone, or conglomerate. There remains little doubt that diamonds have also been obtained artificially, but, owing to our inability to cause the formation to take place under proper physical conditions, or to their too rapid formation, diamonds of very small size only have been thus far obtained.

Diamonds are usually colorless or slightly yellowish, sometimes yellow, blue, green, pink, brown, or black. The more faintly colored are transparent and have a brilliant lustre or fire, which is enhanced by the operation of *cutting* and polishing, which consists in multiplying the num-

ber of facets, or surfaces, of the stone, by holding it, suitably supported, in contact with a quickly revolving metal plate, coated with oil and diamond dust.

The diamond refracts light to a greater degree than any other transparent solid, and it is chiefly to this property that its great brilliancy is due. Its index of refraction is 2.47 to 2.75.

It is the hardest known substance, the solid approaching it most nearly in this respect being crystallized boron. It is very brittle, a bad conductor of heat and of electricity; sp. gr. 3.50 to 3.55. When very strongly heated in vacuo it swells up, leaving a black mass resembling coke; if heated in oxygen it ignites and unites with the oxygen to form carbon dioxide.

Diamonds, whose size, color, or imperfections render them unfit for purposes of luxury, are known as *bort*, and are used, either whole or powdered, for a variety of purposes in the arts where great hardness is required, as in the polishing, drilling, etc., of diamonds and other hard stones, in dressing millstones, in cutting glass, etc.

In weighing diamonds a special arbitrary unit, called the *carat*, is used, which is equivalent to four troy grains, or about 0.25 gram. In the cutting a diamond loses two-thirds or more of its weight. The largest cut diamond known is the Orloff, belonging to the Emperor of Russia, which weighs one hundred and ninety-five carats (one and five-eighths ounce); it is said to have weighed before cutting seven hundred and seventy-nine carats, or nearly six and one-half ounces.

The diamond is almost pure carbon, containing a mere trace of silex and ferric oxide.

Graphite.—A variety of carbon, almost as free from foreign admixture as is the diamond, and like it, occurring in the crystalline form, yet widely differing from it in its physical properties.

It is soft enough to be scratched by the nail; crystallizes in hexagonal plates; is opaque and of a dark gray color, is greasy to the touch, and stains any light-colored substance upon which it is rubbed; is a good conductor of electricity, and a better conductor of heat than the diamond. It contains from one to two per cent. of impurities.

Graphite has been obtained artificially. Molten cast-iron dissolves carbon to a limited extent, and, if it be allowed to cool slowly, the carbon separates in the form of crystals, identical in appearance and properties with those of native graphite. These crystals may be separated from the iron by dissolving the latter in hydrochloric acid.

Graphite is extensively mined in England, Siberia, and the United States, and is used in the arts, under the names *black lead* and *plumbago*, in the manufacture of pencils, crucibles, stove-polish, etc., and in electrotyping.

Amorphous carbon exists in nature in enormous deposits, the remains of vegetable life of past ages, in the form of the different varieties of coal, which contain from eight to twenty-five per cent. of substances other than carbon. *Anthracite* coal is hard and dense; it does not flame when burning; is difficult to kindle, but gives great heat with a suitable draught. It contains eighty to ninety per cent. of carbon, and is sometimes known as stone-coal. *Bituminous* coal varies greatly in appearance, and differs from anthracite in that, when burning, it gives off gases which produce a flame. Some varieties are quite soft, while others, such as *jet*, which is a kind of lignite, are hard enough to assume a high polish. It is usually compact in texture, and very frequently contains im-

pressions of leaves, fruits, and other parts of vegetables. It contains about seventy-five per cent. of carbon.

Besides these forms in which carbon occurs in nature, it is artificially prepared for use in the arts, by the decomposition of substances rich in carbon. The kinds of artificial coal differ from each other according to the different composition of the substances in whose decomposition they have their origin. Ordinary, or vegetable *charcoal*, is obtained by burning woody fibre with an insufficient supply of air, either incidentally in the distillation of wood, or as a separate industry. It is brittle and sonorous; has the form of the wood from which it was obtained, and retains all the mineral matter present in the woody tissue. Its specific gravity is about 1.57. It has the power of condensing within its pores odorous substances and large quantities of gases: 90 volumes of ammonia, 55 of hydrogen sulphide, 9.25 of oxygen. This property is taken advantage of in a variety of ways. Its power of absorbing odorous bodies renders it valuable as a disinfecting and filtering agent, and in the prevention of putrefaction and fermentation of certain liquids. It is with this view that the interiors of barrels intended to hold wine, beer, or water, are carbonized. Certain odorous culinary operations are rendered inodorous by the introduction of a fragment of charcoal into the pot. The efficacy of charcoal as a filtering material is due also, in a great measure, to the oxidizing action of the oxygen condensed in its pores; indeed, if charcoal be boiled with dilute hydrochloric acid, dried, and heated to redness, the oxidizing action of the oxygen, which it thus condenses, is very energetic.

Lamp-black is obtained by incomplete combustion of some resinous or tarry substance, the smoke or soot from which is directed into suitable condensing-chambers. It is a light, amorphous powder, and contains a notable quantity of oily and tarry material, from which it may be freed by heating in a covered vessel. It is used in the manufacture of printer's ink.

Coke is the substance remaining in gas-retorts after the distillation of bituminous coal in the manufacture of illuminating-gas. As all substances capable of yielding gases when heated have been driven off, coke does not possess the property of flaming when burned. It is a hard, grayish substance, usually very porous, dense, and sonorous. When iron retorts are used, a portion of the gaseous products are decomposed by contact with the hot iron surface, upon which there is then deposited a layer of very hard, compact, grayish carbon, which is a good conductor of electricity, and furnishes the best material for making the carbons of galvanic batteries and the points for the electric light. It does not form when gas is made in clay retorts.

Animal charcoal is obtained by calcining animal matters in closed vessels; if prepared from bones it is known as *bone-black;* if from ivory, *ivory-black;* the latter is used as a pigment, the former as a decolorizing agent. Bones yield about sixty per cent. of bone-black, which contains, besides carbon, nitrogen and the phosphates, and other mineral substances of the bones. It possesses in a remarkable degree the power of absorbing coloring matters, for which purpose it is largely used in sugar-refining. When its decolorizing power is lost by saturation with pigmentary bodies, it may be restored, although not completely, by calcination. For certain purposes in the laboratory purified animal charcoal, *i. e.*, freed from mineral matter, is required, and is obtained by extracting the commercial article with hydrochloric acid and washing it thoroughly; its decolorizing

power is diminished by this treatment. Animal charcoal has the power of removing from a solution certain crystalline substances, notably the alkaloids, and a method has been suggested for separating these bodies from organic mixtures by its use.

The most notable chemical property of carbon is the readiness with which it unites with oxygen at high temperatures—a property of the element not only in its three simple forms, but also in most of its compounds. The product of the union is carbon dioxide, if the supply of oxygen is sufficient; if oxygen be present in more limited quantity, carbon monoxide is formed.

The affinity of carbon for oxygen renders it a most valuable reducing agent. Many oxides, when heated with charcoal, are reduced with formation of carbon dioxide:

$$\underset{\text{Cupric oxide.}}{2CuO} + \underset{\text{Carbon.}}{C} = \underset{\text{Copper.}}{2Cu} + \underset{\text{Carbon dioxide.}}{CO_2}$$

The reducing power of oxygen is utilized in many processes in the arts, as in the working of iron and other ores.

If a current of steam be passed over strongly heated coke, the watery vapor is reduced, hydrogen and carbon monoxide being formed—

$$H_2O + C = CO + H_2,$$

a reaction utilized in the manufacture of an illuminating gas, known as water-gas.

At elevated temperatures, about 1000°, carbon also unites directly with sulphur to form a volatile liquid—carbon disulphide.

COMPOUNDS OF CARBON.

Organic Substances.

In the seventeenth and eighteenth centuries, chemists had observed that there might be extracted from animal and vegetable bodies substances which differed much in their properties from those which could be obtained from the mineral world; substances which burned without leaving a residue, and many of which were subject to the peculiar changes wrought by the processes of fermentation and putrefaction. It was not until the beginning of the present century, however, that chemistry was divided into the two sections of *inorganic* and *organic*.

In the latter class were included all such substances as existed only in the organized bodies of animals and vegetables, and which seemed to be of a different essence from that of mineral bodies, as chemists had been unable to produce any of these organic substances by artificial means. Later in the history of the science it was found that these bodies were all made up of a very few elements, and that they all contained carbon. Gmelin at this time proposed to consider as organic substances all such as contained more than one atom of carbon, his object in thus limiting the minimum number of atoms of carbon being that substances containing one atom of carbon, such as carbonic acid and marsh-gas, were formed in the mineral kingdom, and consequently, according to then existing views, could not be considered as *organic*. Illogical as such a distinction is, we find it still adhered to in text-books of very recent date.

The notion that organic substances could only be formed by some mysterious agency, existing only in organized beings, was finally exploded by the labors of Wöhler and Kolbe. The former obtained urea from ammonium cyanate; while the latter, at a subsequent period, formed acetic acid, using in its preparation only such unmistakably mineral substances as coal, sulphur, aqua regia, and water.

During the half-century following Wöhler's first synthesis, chemists have succeeded not only in making from mineral materials many of the substances previously only formed in the laboratory of nature, but have also produced a vast number of carbon compounds which were previously unknown, and which, so far as we know, have no existence in nature. At the present time, therefor, we must consider as an organic substance any compound containing carbon, whatever may be its origin and whatever its properties. Indeed, the name *organic* is retained merely as a matter of convenience, and not in any way as indicating the origin of these compounds. Although, owing to the great number of the carbon compounds, it is still convenient to treat of them as forming a section by themselves, their relations with the compounds of other elements is frequently very close; indeed, within the past few years, compounds of silicon have been obtained, which indicate the possibility that that element is capable of forming series of compounds as interesting in numbers and variety as those of carbon.

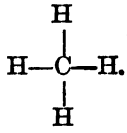
Nevertheless, there are certain peculiarities exhibited by carbon in its compounds, which are not possessed to a like extent by any other element,

and which render the study of organic substances peculiarly interesting and profitable.

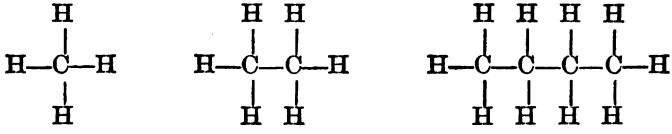
In the study of the compounds of the other elements, we have to deal with a small number of substances, relatively speaking, formed by the union with each other of a large number of elements. With the organic substances the reverse is the case; for, although compounds have been formed which contain carbon along with each of the other elements, the great majority of the organic substances are made up of carbon, combined with a very few other elements, hydrogen, oxygen, and nitrogen occurring in them most frequently.

It is chiefly in the study of the carbon compounds that we have to deal with *radicals* (see p. 17). Among mineral substances there are many whose molecules consist simply of a combination of two atoms; among organic substances there is none which does not contain a radical; indeed, organic chemistry has been defined as "the chemistry of compound radicals."

The atoms of carbon possess in a higher degree than those of any other element, silicon possibly excepted, the power of uniting with each other, and in so doing of interchanging valences. Were it not for this property of the carbon atoms, we could have but one saturated compound of carbon and hydrogen, CH_4, or, expressed graphically:



There exists, however, a great number of such compounds, which differ from each other by one atom of carbon and two atoms of hydrogen. In these substances the atoms of carbon may be considered as linked together in a continuous chain, their free valences being satisfied by atoms of hydrogen; thus:



If now one atom of hydrogen be removed from either of these combinations, we have a group possessing one free valence, and consequently univalent. The decompositions of these substances show that they contain such radicals, and that their typical formulæ are:

$$\left.\begin{matrix}CH_3\\H\end{matrix}\right\};\qquad \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\};\qquad \left.\begin{matrix}C_4H_9\\H\end{matrix}\right\}.$$

Homologous Series.

It will be observed that these formulæ differ from each other by CH_2, or some multiple of CH_2, more or less. In examining numbers of organic substances, which are closely related to each other in their properties, we

find that we can arrange the great majority of them in series, each term of which differs from the one below it by CH_2; such a series is called an *homologous series*. It will be readily understood that such an arrangement in series vastly facilitates the remembering of the composition of organic bodies. In the following table, for example, are given the saturated hydrocarbons and their more immediate derivatives. At the head of each vertical column is an algebraic formula, which is the general formula of the entire series below it; *n* being equal to the numerical position in the series. The chemist is not obliged to burden his memory with all the formulæ in the table, but simply to remember the algebraic formulæ. The *name* of the substance conveys, in most instances, to his mind the series to which it belongs, and its position in that series; and by the aid of the algebraic formula, or *general formula* as it is called, its composition is found in a moment.

HOMOLOGOUS SERIES.

Saturated hydrocarbons, C_nH_{2n+2}.	Alcohols, $C_nH_{2n+2}O$.	Aldehydes, $C_nH_{2n}O$.	Acids, $C_nH_{2n}O_2$.	Ketones, $C_nH_{2n}O$.
CH_4	CH_4O	.....	CO_2H_2	.....
C_2H_6	C_2H_6O	C_2H_4O	$C_2O_2H_4$	.....
C_3H_8	C_3H_8O	C_3H_6O	$C_3O_2H_6$	C_3H_6O
C_4H_{10}	$C_4H_{10}O$	C_4H_8O	$C_4O_2H_8$	C_4H_8O
C_5H_{12}	$C_5H_{12}O$	$C_5H_{10}O$	$C_5O_2H_{10}$	$C_5H_{10}O$
C_6H_{14}	$C_6H_{14}O$	$C_6H_{12}O$	$C_6O_2H_{12}$	.....
C_7H_{16}	$C_7H_{16}O$	$C_7H_{14}O$	$C_7O_2H_{14}$	.....
C_8H_{18}	$C_8H_{18}O$	$C_8H_{16}O$	$C_8O_2H_{16}$	.....
C_9H_{20}	$C_9H_{20}O$	.....	$C_9O_2H_{18}$	.....
$C_{10}H_{22}$	$C_{10}H_{22}O$	.....	$C_{10}O_2H_{20}$	.....
$C_{11}H_{24}$	.....	.....	.....	.....
$C_{12}H_{26}$	.....	.....	$C_{12}O_2H_{24}$	.....
$C_{13}H_{28}$	.....	.....	.....	.....
$C_{14}H_{30}$	.....	.....	$C_{14}O_2H_{28}$	.....

But the arrangement in homologous series does more for us than this. The properties of substances in the same series vary in regular gradation according to their position in the series; thus, in the series of alcohols in the above table, the boiling-points of the first six are, 66.5°, 78.4°, 96.7°, 111.7°, 132.2°, 153.9°; from which it will be seen that the boiling-point of any one of them can be determined, with a maximum error of 3°, by taking the mean of those of its neighbors above and below. In this way we may prophecy, to some extent, the properties of a wanting member in a series before its discovery. The terms of any homologous series must all have the same *constitution*, *i. e.*, their constituent atoms must be similarly arranged within the molecule.

ISOMERISM—METAMERISM—POLYMERISM.

Two substances are said to be isomeric, or to be isomeres of each other, when, upon analysis, they prove to have the same centesimal composition. If, for instance, we analyze acetic acid and methyl formiate, we find that

each body consists of carbon, oxygen, and hydrogen, in the following proportions:

Carbon	40	$24=12\times2$
Oxygen	53.33	$32=16\times2$
Hydrogen	6.67	$4=4\times1$
	100.00	60

This similarity of centesimal composition may occur in two ways: the two substances may each contain in a molecule the same numbers of each kind of atom; or one may contain in each molecule the same kind of atoms as the other, but in a higher multiple. In the above instance, for example, each substance may have the composition $C_2H_4O_2$; or one may have that formula and the other, $C_6H_{12}O_6$, or $C_2H_4O_2\times3$. In the former case the substances are said to be *metameric*, in the latter *polymeric*. Whether two substances are metameric or polymeric can only be determined by ascertaining the weights of their molecules, which is usually accomplished by determining the specific gravities of their vapors (see p. 14).

The specific gravity of the vapor of acetic acid is the same as that of methyl formiate, and, consequently, each substance is made up of molecules, each containing $C_2H_4O_2$. But the two substances differ from each other greatly in their properties, and their differences are at once indicated by their typical or graphic formulæ:

$$\left.\begin{matrix}(C_2H_3O)'\\H\end{matrix}\right\}O \quad \text{and} \quad \left.\begin{matrix}(CHO)'\\(CH_3)'\end{matrix}\right\}O;$$

or graphically:

$$\begin{matrix}CH_3\\|\\COO.H\end{matrix} \quad \text{and} \quad \begin{matrix}H\\|\\CO.OCH_3.\end{matrix}$$

Polymeric substances, although they yield the same result upon centesimal analysis, possess different molecular weights, that of one being a simple multiple of that of the other. Acetic acid and grape-sugar, on analysis, both prove to have the same centesimal composition:

Carbon	40.	12
Oxygen	53.33	16
Hydrogen	6.67	2
	100.00	30

but the molecular weight of acetic acid is 60, or $12\times2+16\times2+1\times4$, and its composition is therefor $C_2O_2H_4$. The molecule of grape-sugar weighs 180, or $12\times6+16\times6+1\times12$, and its composition is therefor $C_6O_6H_{12}$.

Classification of Organic Substances.

As the compounds of the other elements may be divided into classes, such as acids, bases, salts, etc., according to their chemical functions, the

compounds of carbon also arrange themselves into certain well-defined groups, called by the French chemists *functions*—a term which it would be well to introduce into our own nomenclature. The properties of the functions of organic substances do not depend, like those of other compounds, upon the *kind* of atoms of which they are composed, but rather upon the arrangement of the atoms within the molecule; and in this point we find the most prominent distinction between organic and mineral substances. Arsenic, for instance, is poisonous in whatever form of chemical combination it may be, provided only that it can be rendered soluble, and therefor capable of absorption. Carbon, oxygen, and hydrogen, on the other hand, combine with each other to form substances having the most diverse action upon the economy—the fats and sugars, ordinary articles of food, on the one hand, and substances having such marked toxic powers as ether and oxalic acid, on the other—the differences between the properties of the two substances depending entirely upon the numbers and positions in the molecule of the same kind of atoms.

Before entering upon the consideration of the individual compounds, and to render what follows intelligible, we must briefly describe the general properties of these different functions.

Derivatives of the Saturated Hydrocarbons—Compounds of Univalent Radicals.

Saturated hydrocarbons.—A hydrocarbon is a compound consisting of carbon and hydrogen *only*, and it is *saturated* when all the valences of the constituent atoms are satisfied. These substances belong to the homologous series of which marsh-gas is the first term, and which has the general formula, C_nH_{2n+2}. Like all other saturated compounds, their composition cannot be modified by *addition*, *i. e.*, by the simple insertion of other atoms into the molecule; they may, however, be modified by *substitution*, *i. e.*, by the removal of one or more of their atoms, and the substitution therefor of one or more atoms of a different kind. Their composition is expressed by the typical formula:

$$\left.\begin{matrix} C_nH_{2n+1} \\ H \end{matrix}\right\} \text{ e. g. } \left.\begin{matrix} (CH_3) \\ H \end{matrix}\right\}$$

The groups C_nH_{2n+1}, containing one unsatisfied valence, are univalent, and are the *radicals* of which these hydrocarbons are the *hydrides*. These univalent radicals, more or less modified by substitution, enter into the composition of a vast number of important substances, which are thus said to be *derivatives* of this series of hydrocarbons. These radicals are also sometimes designated as *alcoholic*, as they exist in the series of substances of which ordinary alcohol is the type. The members of this series are sometimes called *paraffines*, from the occurrence of the higher terms in the commercial product of that name and in petroleum.

Chlorides, Bromides, and Iodides.—The radicals of this series behave in many respects like atoms of a univalent, electro-positive element, and, like them, are capable of uniting with an atom of chlorine, bromine, or iodine, to form chlorides, bromides, or iodides.

$$\underset{\text{Ethyl hydride.}}{(C_2H_5)'H} + \underset{\text{Bromine.}}{Br_2} = \underset{\text{Ethyl bromide.}}{(C_2H_5)'Br} + \underset{\text{Hydrogen bromide.}}{BrH}$$

These substances are also designated as *haloid ethers*, corresponding, as they do, with the haloid salts. Several of them are used medicinally.

Alcohols.—The name alcohol, formerly applied only to the substance now popularly so called, has gradually come to be used to designate a large class of important bodies, of which vinic alcohol is the representative. These substances are mainly characterized by their power of entering into double decomposition with acids, to form neutral compounds, called compound ethers, water being at the same time formed, at the expense of both alcohol and acid. They are the hydrates of the alcoholic radicals, and as such resemble the metallic hydrates, while the compound ethers are the counterparts of the metallic salts:

$$\underset{\text{Ethyl hydrate.}}{\left.\begin{matrix}(C_2H_5)\\H\end{matrix}\right\}O} + \underset{\text{Acetic acid.}}{\left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O} = \underset{\text{Ethyl acetate.}}{\left.\begin{matrix}(C_2H_3O)\\C_2H_5\end{matrix}\right\}O} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}$$

$$\underset{\text{Potassium hydrate.}}{\left.\begin{matrix}K\\H\end{matrix}\right\}O} + \underset{\text{Acetic acid.}}{\left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O} = \underset{\text{Potassium acetate.}}{\left.\begin{matrix}(C_2H_3O)\\K\end{matrix}\right\}O} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}$$

As the metallic hydrates may be considered as formed by the union of one atom of the metallic element with a number of groups OH′, corresponding to its valence, so the alcohols are formed by union of an unoxidized radical with a number of groups OH′, equal to or less than the number of free valences of the radical. When the alcohol contains one OH, it is designated as *monoatomic;* when two, *diatomic;* when three, *triatomic,* etc.

The simplest alcohols are those derivable from the saturated hydrocarbons, and having the general formula $C_nH_{2n+2}O$, or $C_nH_{2n+1}OH$. The terms of this series, which contains vinic alcohol, may be formed synthetically:

First.—By acting upon the corresponding iodide with potassium hydrate:

$$C_2H_5I + KHO = KI + C_2H_5OH.$$

Second.—From the alcohol next below it in the series, by direct addition of CH_2, only, however, by a succession of five reactions.

Third.—By the action of sulphuric acid and water upon the corresponding hydrocarbon of the series C_nH_{2n}.

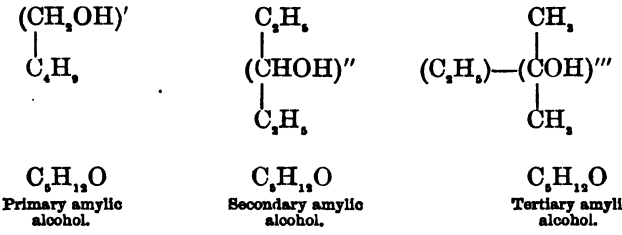
The saturated monoatomic alcohols are, however, not limited to one corresponding to each alcoholic radical. It has been found that there exist—corresponding to the higher alcohols—a number of substances having the same centesimal composition and the same alcoholic properties, and differing only in their physical characters and in their products of decomposition and oxidation. These isomeres have been the subject of much careful study of late years. It has been found that the molecules of methyl, ethyl, and other higher alcohols are made up of the group $(CH_2OH)'$ united to H or to C_nH_{2n+1}, thus:

CH_2OH	CH_2OH	CH_2OH
|	|	|
H	CH_3	C_2H_5
Methyl alcohol.	Ethyl alcohol.	Propyl alcohol.

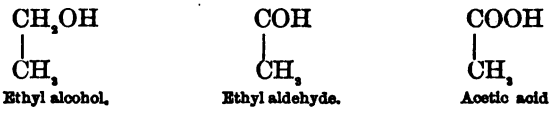
and all monoatomic alcohols containing this group, CH_2OH, have been designated as *primary alcohols*. Isomeric with these are other bodies, which, in place of the group $(CH_2OH)'$, contain the group $(CHOH)''$, which are distinguished as *secondary alcohols*. Thus we have:



And, further, other substances are known, which contain the group $(COH)'''$, and which are called *tertiary alcohols*, thus:



The alcohols of these three classes are distinguished from each other principally by their products of oxidation. The primary alcohols yield by oxidation, first an aldehyde and then an acid, each containing the same number of atoms of carbon as the alcohol, and formed, the aldehyde by the removal of H_2 from the group (CH_2OH), and the acid by the substitution of O for H_2 in the same group, thus:



In the case of the secondary alcohols, the first product of oxidation is a *ketone*, containing the same number of atoms of carbon as the alcohol, and formed by the substitution of O for HOH in the distinguishing group:



The tertiary alcohols yield by oxidation ketones or acids, whose molecules contain a less number of atoms of carbon than the alcohol from which they are derived.

But the complication does not end here; isomeres have been found to exist corresponding to the higher alcohols, which are themselves primary alcohols, and contain the group $(CH_2OH)'$. It has been shown by recent investigation that there exist no less than seven distinct substances, all having the centesimal composition of amyl alcohol, $C_5H_{12}O$, and the properties of alcohols; and theoretical considerations point to the probable existence of an eighth. Of these eight substances, four are primary, three secondary alcohols, and the remaining one a tertiary alcohol. As each of these bodies contains the group of atoms characteristic of the class of alcohol to which it belongs, it is obvious that the differences observed in their properties are due to differences in the arrangement of the other atoms of the molecule. Experimental evidence, which it would require too much space to discuss in this place, has led chemists to ascribe the following formulæ of constitution to these isomeres:

Primary amylic alcohols:

$$CH_3—CH_2—CH_2—CH_2—CH_2,OH$$

Normal amylic alcohol.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\rangle CH—CH_2—CH_2,OH$$

Active amylic alcohol of fermentation.

$$CH_3—CH_2\!\!\begin{matrix} CH_3 \\ \rangle \end{matrix}\!\!CH—CH_2,OH$$

Inactive amylic alcohol of fermentation.

$$\begin{matrix} CH_3 \\ CH_3—C—CH_2,OH \\ CH_3 \end{matrix}$$

Unknown.

Secondary amylic alcohols:

$$\begin{matrix} CH_3—CH_2 \\ CH_3—CH_2 \end{matrix}\!\!\rangle CH,OH$$

Diethyl carbinol.

$$CH_3—CH_2—CH_2\!\!\begin{matrix} CH_3 \\ \rangle \end{matrix}\!\!CH,OH$$

Methyl-propyl carbinol.

$$\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\!\!\rangle CH,OH$$

Methyl-isopropyl carbinol.

Tertiary amyl alcohol:

$$\begin{matrix} CH_3 \\ CH_3—C,OH \\ CH_3—CH_2 \end{matrix}$$

For alcohols of other series, see pp. 230, 274.

Simple Ethers.—These bodies are the oxides of the alcoholic radicals,

and in constitution bear the same relation to the alcohols that the oxides of basylous elements bear to their hydrates:

$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$ Ethyl oxide (ethylic ether).

$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$ Ethyl hydrate (alcohol).

$\left.\begin{matrix}K\\K\end{matrix}\right\}O$ Potassium oxide.

$\left.\begin{matrix}K\\H\end{matrix}\right\}O$ Potassium hydrate.

When the two alcoholic radicals are the same, as in the above instance, the ether is designated as simple; when they are different, as in methyl-ethyl oxide, $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$, they are called *mixed ethers*.

Monobasic Acids.—By the action of oxidants upon the primary monoatomic alcohols, one atom of oxygen is substituted for H_2 in the group CH_2OH, with the formation of substances having the functions of acids, and containing in each molecule one atom of replaceable hydrogen:

$CH_3—CH_2—CH_2—CH_2—CH_2,OH$
Normal amylic alcohol.

$CH_3—CH_2—CH_2—CH_2—CO,OH$
Normal valerianic acid.

The introduction of the atom of oxygen communicates electro-negative qualities to that portion of the molecule other than OH, to the radical; in other words:

$\left.\begin{matrix}C_5H_{11},\\H\end{matrix}\right\}O$ Amylic alcohol.

$\left.\begin{matrix}C_5H_9O\\H\end{matrix}\right\}O$ Valerianic acid.

And it is to this electro-negative nature of the radical, that the substance owes its acid nature.

The acids formed by the oxidation of the primary alcohols, have the general formula

$$C_nH_{2n}O_2, \quad \text{or} \quad \left.\begin{matrix}C_nH_{2n-1}O\\H\end{matrix}\right\}O$$

Compound Ethers.—As the alcohols resemble the mineral bases, and the organic acids resemble those of mineral origin, so the compound ethers are similar in constitution to the salts, being formed by the double decomposition of an alcohol with an acid, mineral or organic, as a salt is formed by double decomposition of an acid and a mineral base, the radical playing the part of an atom of corresponding valence.

$\left.\begin{matrix}K'\\H\end{matrix}\right\}O$ Potassium hydrate. $+$ $\left.\begin{matrix}(NO_2)\\H\end{matrix}\right\}O$ Nitric acid. $=$ $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ Water. $+$ $\left.\begin{matrix}(NO_2)\\K'\end{matrix}\right\}O$ Potassium nitrate.

$$\underset{\text{Ethyl hydrate (alcohol).}}{(C_2H_5)'\left.\begin{matrix}\\H\end{matrix}\right\}O} + \underset{\text{Nitric acid.}}{(NO_2)\left.\begin{matrix}\\H\end{matrix}\right\}O} = \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} + \underset{\text{Ethyl nitrate (nitric ether).}}{\left.\begin{matrix}(NO_2)\\(C_2H_5)'\end{matrix}\right\}O}$$

$$\underset{\text{Ethyl hydrate.}}{(C_2H_5)'\left.\begin{matrix}\\H\end{matrix}\right\}O} + \underset{\text{Acetic acid.}}{(C_2H_3O)'\left.\begin{matrix}\\H\end{matrix}\right\}O} = \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} + \underset{\text{Ethyl acetate (acetic ether).}}{\left.\begin{matrix}(C_2H_3O)'\\(C_2H_5)'\end{matrix}\right\}O}$$

Aldehydes. — It will be remembered that the monobasic acids are obtained from the alcohols by oxidation of the radical:

$$\underset{\text{Ethyl alcohol.}}{(C_2H_5)\left.\begin{matrix}\\H\end{matrix}\right\}O} \qquad \underset{\text{Acetic acid.}}{(C_2H_3O)'\left.\begin{matrix}\\H\end{matrix}\right\}O}$$

These oxidized radicals are capable of forming compounds similar in constitution to those of the non-oxidized radicals. There are chlorides, bromides, and iodides; their hydrates are the *acids*, $(C_2H_3O)\left.\begin{matrix}\\H\end{matrix}\right\}O$, = acetic acid; their oxides are known as *anhydrides*, $\left.\begin{matrix}(C_2H_3O)\\(C_2H_3O)\end{matrix}\right\}O$ = acetic anhydride; and their hydrides are the *aldehydes* $(C_2H_3O)\left.\begin{matrix}\\H\end{matrix}\right\}$ = acetic aldehyde, the name aldehyde being a corruption of *alcohol dehydrogenatum*, from the method of their formation, by the removal of hydrogen from alcohol.

The aldehydes all contain the group of atoms $(COH)'$, and their constitution may be thus graphically indicated:

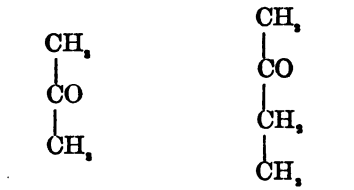
$$\underset{\text{Acetic aldehyde.}}{\begin{matrix}COH\\|\\CH_3\end{matrix}} \qquad \underset{\text{Propionic aldehyde.}}{\begin{matrix}COH\\|\\CH_2\\|\\CH_3\end{matrix}}$$

They are capable, by fixing H_2, of regenerating the alcohol; and, by fixing O, of forming the corresponding acid:

$$\underset{\text{Acetic aldehyde.}}{\begin{matrix}COH\\|\\CH_3\end{matrix}} \qquad \underset{\text{Ethylic alcohol.}}{\begin{matrix}CH_2OH\\|\\CH_3\end{matrix}} \qquad \underset{\text{Acetic acid.}}{\begin{matrix}CO,OH\\|\\CH_3\end{matrix}}$$

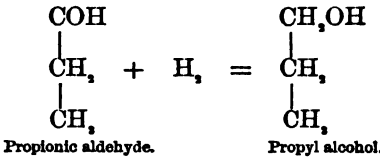
Ketones or Acetones.—Although the aldehydes are not acid in reaction, and are not usually regarded as acids, there exists a number of substances known as ketones or acetones, which may be regarded as formed by the substitution of an alcoholic radical for the hydrogen of the group COH.

These substances all contain the group of atoms (CO)″, and their constitution may be represented graphically thus :

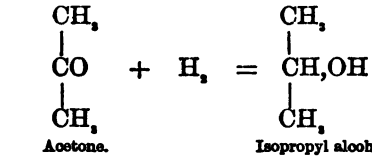


Dimethyl ketone (acetone). Methyl-ethyl ketone.

The first being a symmetrical ketone and the latter a non-symmetrical. The ketones are isomeric with the aldehydes, from which they are distinguished : 1st, by the action of hydrogen, which produces a primary alcohol with an aldehyde, and a secondary alcohol with a ketone:

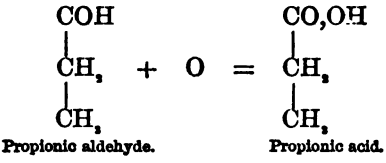


Propionic aldehyde. Propyl alcohol.

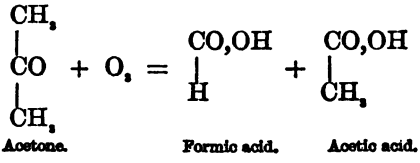


Acetone. Isopropyl alcohol.

2d, by the action of oxygen, which unites directly with an aldehyde to produce the corresponding acid, while it causes the disruption of the molecule of a ketone, with formation of two acids:



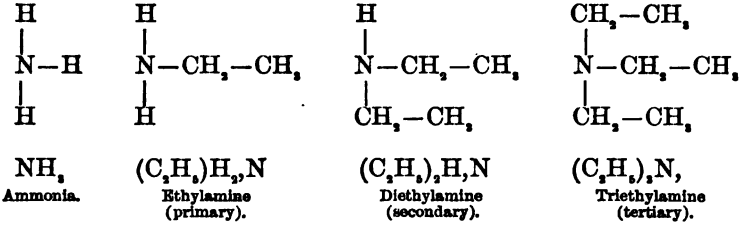
Propionic aldehyde. Propionic acid.



Acetone. Formic acid. Acetic acid.

Amines or compound ammonias. — The *monamines* are substances which may be considered as being derived from one molecule of ammonia by the substitution of one, two, or three alcoholic radicals for one, two, or

three atoms of hydrogen. They are designated as *primary*, *secondary*, and *tertiary*, according as they contain one, two, or three alcoholic radicals:



These bodies closely resemble ammonia in their chemical properties; they unite with acids, without elimination of water, to form salts resembling those of ammonium. They also unite with water to form compounds, called quaternary ammonium hydrates, similar in constitution to ammonium hydrate.

Although the amines of this series are chiefly of theoretical interest, other series contain substances of great practical importance (see p. 346).

Amides.—These bodies differ from the amines in containing *oxygenated*, or *acid* radicals, in place of alcoholic radicals. Like the amines, they are divisible into *primary*, *secondary*, and *tertiary*. They are the nitrides of the acid radicals, as the amines are the nitrides of the alcoholic radicals.

The monamides may also be regarded as the acids in which the OH of the group COOH has been replaced by (NH_2):



(For other amides see p. 256.)

Amido-acids or Glycocols.—These are compounds of mixed function, obtained by the substitution of the univalent group $(NH_2)'$, for an atom of radical hydrogen of an acid:



Some of them, and many of their derivatives, exist in animal bodies. Corresponding to them are many isomeres belonging to other series.

SATURATED HYDROCARBONS.

SERIES C_nH_{2n+2}.

The members of this series are the most simply constituted of organic substances. They exist in nature chiefly as products of what is commonly regarded as the mineral kingdom, and constitute the inflammable gases and rock-oils which issue from the earth in Pennsylvania, Russia, and other places.

The following is a list of the members of this group at present known:

Name.	Formula.	Specific gravity of liquid.	Boiling-point. Centigrade.
Methyl hydride	CH_3H	.....	.....
Ethyl hydride	C_2H_5H	.....	.....
Propyl hydride	C_3H_7H	.....	.....
Butyl hydride	C_4H_9H	0.600 at 0°	0°
Amyl hydride	$C_5H_{11}H$	0.628 at 18°	30°
Hexyl hydride	$C_6H_{13}H$	0.669 at 18°	68°
Heptyl hydride	$C_7H_{15}H$	0.690 at 18°	92°—94°
Octyl hydride	$C_8H_{17}H$	0.726 at 18°	116°—118°
Nonyl hydride.....	$C_9H_{19}H$	0.741 at 18°	136°—138°
Decyl hydride	$C_{10}H_{21}H$	0.757 at 18°	158°—162°
Undecyl hydride	$C_{11}H_{23}H$	0.766 at 18°	180°—182°
Dodecyl hydride	$C_{12}H_{25}H$	0.778 at 18°	198°—200°
Tridecyl hydride	$C_{13}H_{27}H$	0.796 at 18°	218°—220°
Tetradecyl hydride	$C_{14}H_{29}H$	0.809 at 18°	236°—240°
Pentadecyl hydride.....	$C_{15}H_{31}H$	0.825 at 18°	258°—262°
Hexadecyl hydride	$C_{16}H_{33}H$	.....	about 280°

Methyl Hydride.

Methane—Marsh-gas—Light carburetted hydrogen—Fire-damp—CH_4 or $\left.\begin{matrix}(CH_3)\\H\end{matrix}\right\}$.—It is given off from decomposing vegetable matter in swamps and bogs. Volta, in 1778, first recognized the individuality of the inflammable gas observed in such situations.

The *fire-damp*, which has been the cause of such terrible loss of life in coal-mines, is a mixture composed almost entirely of methyl hydride and air, in varying proportions. In many localities in the vicinity of coal or petroleum deposits, and in some instances at considerable distances from such formations, there issue large volumes of inflammable gases from fissures and borings in the earth. These gases consist of methyl hydride, mixed with the higher members of the series. If the latter be present in notable proportions, the flame of the gas is luminous, and may be utilized for illuminating purposes. Illuminating gas, obtained from

the distillation of coal, contains from thirty-six to fifty per cent. of this gas (see p. 287).

When desired in a state of purity, marsh-gas is best obtained by heating strongly a mixture of sodium acetate and sodium hydrate, each one part, and quicklime one and one-half parts, and collecting the gas over water:

$$C_2H_3O_2Na+NaHO=CO_3Na_2+CH_4.$$

Methyl hydride is a colorless, odorless, tasteless gas; very sparingly soluble in water; more soluble in alcohol; sp. gr. 0.559A.

Like all the members of this series, marsh-gas is a very stable substance, and is not readily attacked by reagents; it is for this reason that the name *paraffines* (from *parum*, little, and *affinis*, related to by marriage) has been applied, particularly to the higher terms of the series, and recently to the entire series.

At high temperatures it is decomposed into carbon and hydrogen:

$$CH_4=C+2H_2.$$

Its decomposition takes place at much lower, but still elevated, temperatures when it is mixed with air or oxygen. It burns in air with a pale yellow flame, which is extinguished when cooled. Advantage is taken of this in the construction of miners' safety-lamps, in which the flame is enclosed in a cage of fine wire-gauze, which, by its cooling effect, prevents the transmission of flame from the lamp outward. If a mixture of marsh-gas and oxygen (or air) be heated at a single point by the passage of the electric spark, or by the approach of a flame, instant decomposition of the entire mass takes place, with a violent explosion, and the formation of carbon dioxide and water:

$$CH_4+2O_2=CO_2+2H_2O.$$

The formation of immense volumes of carbon dioxide in this way, in mine-explosions, produces what is known to miners as *after-damp*, usually fatal to those who have escaped the violence of the explosion itself.

Chlorine has no action upon marsh-gas in the dark and cold; under the influence of diffuse daylight, however, one or more of the atoms of hydrogen are replaced by an equivalent quantity of chlorine. In direct sunlight the change takes place with an explosion. The higher terms of this series are of interest principally as constituting petroleum and allied bodies obtained therefrom.

Petroleum.

(From *πέτρα*, a rock, and *oleum*, oil.) Mineral oils have been known from the remotest antiquity, and were obtained from the vicinity of Agrigentum, in Sicily, from the Island of Zacynthus, in the Ionian Sea, and from Persia, for use as a medicine and for burning in lamps. In later times petroleum was found in various parts of Europe, Asia, and South and North America. It is only, however, since 1859 that rock-oil has become the commercially important substance that it now is. In 1853 attention was first drawn to the existence of petroleum in Pennsylvania, and from that date until 1859 attempts were made to obtain the oil by the old

Indian method of sinking square pits into the earth, in which cloths were then placed until saturated with the oil, which was then wrung out.

In 1859 the *oil fever* was inaugurated with the sinking of a well seventy-five feet deep near Titusville, from which ten barrels or four hundred and thirty gallons of oil were obtained daily. A great number of wells were now sunk at various points in the Oil Creek Valley, and with such success that the production during the first year amounted to eighty-two thousand barrels, or over three and one-half millions of gallons. From that time to the present the production of oil has steadily increased.

The production is not limited to Pennsylvania, large quantities being obtained from Ohio, Western New York, West Virginia, Lower Canada, as well as from California, Burmah, Borneo, and the shores of the Caspian Sea. The oil obtained in different localities varies in composition. In the American oil districts the oil is obtained from either *flowing* or *pumping* wells, the former of which yield enormous quantities of oil, but cease flowing after a time. The famous Empire well flowed from 1862 to 1866, and yielded two thousand barrels, or eighty-six thousand gallons, per diem. In its deposits the oil is associated with salt water and gaseous hydrocarbons, forming a layer upon the surface of the water. When the deposit occurs in a closed *pocket*, the pressure of the gas is sufficient to force through a tube penetrating the cavity either water, oil, or gas, as the end of the tube is in one or another layer.

The crude petroleum, as it comes from the well, is a highly inflammable substance, differing in composition and in physical properties in the products of different wells, even in the same section of country. It varies in color from a faintly yellowish tinge to a dark brown, nearly black, with greenish reflections. The lighter-colored varieties are limpid, and the more highly colored of the consistency of thin syrup. The specific gravity varies from 0.74 to 0.92. The composition of crude petroleums has been the subject of a great deal of investigation; they have been found to contain all the hydrocarbons mentioned in the list on p. 157, (the first of the series, being found in the gases accompanying petroleum, is also held in solution by the oil under the pressure it supports in natural pockets), besides hydrocarbons of the olefine series (see p. 227), and of the benzol series (see p. 315).

The crude oil is highly inflammable, usually highly colored, and is prepared for its multitudinous uses in the arts by the processes of distillation and refining; which, in the case of the American oils, are conducted at the three principal refineries at Cleveland, O., New York, and Pittsburg, Pa., to which points the mixed oils from various wells are conveyed by boat, rail, or lines of pipes.

The process of distillation is usually so conducted as to divide the crude oil into four parts:

Naphtha.....	sp. gr. 0.700 at 15° C.	12—15 per cent.
Benzine	sp. gr. 0.730 at 15° C.	9—12 per cent.
Burning-oil....	sp. gr. 0.783 at 15° C. about	60 per cent.
Residuum and loss.....		about 13—19 per cent.

The *naphtha*, also known as petroleum ether, is by further fractional distillation again subdivided into other products:

Rhigolene, a highly volatile and inflammable liquid, which boils at 21° C.=70° F., and has a specific gravity of about 0.60=90°—97° Baumé. It has been used as a substitute for ether to produce cold by

evaporation. It should be kept in a situation where the temperature does not rise above its boiling-point, and should be handled with caution, as its vapor forms an explosive mixture with air.

Gasoline, also obtained from naphtha, boils at 76.6° C.=170° F., and has a specific gravity of 0.63—0.61=80°—90° Baumé, and is used, as its name implies, for the manufacture of illuminating gas.

Benzine, or *benzoline*, is a colorless liquid, boiling at 148° C.=298° F., having a specific gravity of 0.73=60° Baumé, and a peculiar odor. It is largely used in the arts as a solvent for fatty substances. It must not be confounded with benzene or benzol, which is a totally different substance, obtained from coal-tar (see p. 315). The two substances resemble each other in appearance, but may be distinguished by the following characters:

BENZOLINE.	BENZENE.
Boils at about 140° C., sp. gr. 0.69—0.73, or 60° to 70° Baumé; does not crystallize at the freezing-point of water.	Boils at 80° C., sp. gr. 0.88, or 30° Baumé; crystallizes at 3.2° C.
Smells of petr leum; does not sensibly dissolve pitch or absolute carbolic acid in the cold.	Smells of coal-tar; dissolves pitch readily, forming a dark brown solution. Is miscible with absolute carbolic acid in all proportions.

The most important product of petroleum is that portion which passes over at temperatures above 183° C., and which constitutes what is usually known as *kerosene*—various other trade-names being applied to it in different degrees of purity, and by different manufacturers. In the manufacture of these burning-oils care must be had that the more volatile compounds are separated, and that the temperature be not pushed too high; in the latter case the oil is "cracked," *i. e.*, the denser oils remaining in the still are dissociated, forming highly volatile compounds, which mix with the product. In either case the kerosene is liable to give rise to accidents, either by igniting, in case the lamp is broken or overturned, and, in very bad oils, by forming with air a mixture which may explode the lamp. In order to guard against such accidents, laws have gradually been framed in various States and countries, regulating the manufacture, transportation, and storage of these oils. The tests to which they are subjected relate to the temperature at which they give off inflammable vapors and that at which they ignite. The tests are applied by gradually warming the oil, and noting the temperature, indicated by a thermometer plunged in it, at the time when a lighted match, carried over its surface, produces a flash, and the temperature when the oil itself ignites; the former is known as the "flashing-point," the latter as the "burning-point;" the former is about 5°—8° C.=10°—15° F. below the latter. It was formerly supposed that an oil flashing at 43° C.=110° F. was safe; but subsequent experience has shown that kerosene gives off explosive vapors at a temperature 5°—8° C.=10°—15° F. below its flash-point, and 14°—17° C.=25°—30° F. below its burning-point, and serious accidents have resulted from the use of oils of 110° flash. A kerosene is now required, therefor, to have a flash-point of 60° C.=140° F., and a burning-point of 65.5C.=150° F.; an oil of lower test is unsafe.

If the oil be colored, as is usually the case, it is purified—refined—by heating with sulphuric acid, and then with caustic soda. The neighborhood of petroleum refineries, as residents of New York are aware, is frequently infected with disgusting and deleterious odors, emanating

partly from the waste acid used in the refining, and partly from the vapors issuing from the stills when the oil is purposely "cracked," that a greater yield of kerosene may be obtained.

From the residue remaining after the separation of the kerosene, a variety of other products are obtained. *Lubricating oils*, of too high boiling-point for use in lamps. *Paraffine*, a white, crystalline solid, fusible at 45°—65°, which is used in the arts for a variety of purposes formerly served by wax, such as the manufacture of candles. In the laboratory it is very useful for coating the glass stoppers of bottles, and for other purposes, as it is not affected by acids or by alkalies. It is odorless, tasteless, insoluble in water and in cold alcohol; soluble in boiling alcohol and in ether, fatty and volatile oils, and mineral oils. It is also obtained by the distillation of certain varieties of coal, and is found in nature in fossil wax or ozocerite.

The products known as *vaseline, cosmoline*, etc., which are now so largely used in pharmacy and perfumery, are mixtures of paraffine and the heavier petroleum oils. Like petroleum itself, its various commercial derivatives are not definite compounds, but mixtures of the hydrocarbons of this series.

CHLORINE, BROMINE, AND IODINE DERIVATIVES OF HYDROCARBONS OF THE SERIES C_nH_{2n+2}.

By the action of bromine upon the hydrocarbons of this series, or by the action of hydrochloric, hydrobromic, or hydriodic acid upon the corresponding hydrate, compounds are obtained in which one atom of hydrogen of the hydrocarbon is replaced by an atom of chlorine, bromine, or iodine:

$$\underset{\text{Ethyl hydride.}}{C_2H_6} + \underset{\text{Bromine.}}{Br_2} = \underset{\text{Ethyl bromine.}}{C_2H_5Br} + \underset{\text{Hydrobromic acid.}}{HBr},$$

$$\underset{\text{Ethyl hydrate.}}{C_2H_5OH} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ethyl chloride.}}{C_2H_5Cl} + \underset{\text{Water.}}{H_2O},$$

These substances are also known as haloid ethers.

Methyl Chloride—CH_3Cl,

Is obtained as a colorless gas, slightly soluble in water, and having a sweetish odor and taste, by distilling together sulphuric acid, sodium chloride, and methylic alcohol; also, on a commercial scale, from the residues of the manufacture of beet-sugar. Under the influence of cold it forms a liquid which boils at −22°.

It is inflammable, and burns with a greenish flame. When mixed with chlorine and exposed to sunlight, a further substitution of chlorine for hydrogen takes place. When heated with potassium hydrate, it is converted into methyl hydrate.

Methyl Bromide—CH_3Br.

A colorless liquid; boils at 13°; sp. gr. 1.664; has an ethereal and faintly alliaceous odor; prepared by the combined action of phosphorus and bromine upon methyl hydrate.

Methyl Iodide—CH_3I.

A colorless liquid; boils at about 45°; sp. gr. 2.237; burns with difficulty, giving off violet vapors of iodine. It is prepared by a process similar to that used for obtaining the bromide. It is used in the laboratory, for the introduction of radical methyl into other compounds; and in the arts, in the manufacture of aniline colors.

Ethyl Chloride.

Hydrochloric or muriatic ether, C_2H_5Cl.—A colorless, mobile liquid; boils at 11°; has an agreeable odor; burns with a greenish flame. It is obtained by passing hydrochloric acid gas through ethylic alcohol to saturation, and distilling over the water-bath. It is used in medicine in alcoholic solution; it also exists in *tr. ferri chloridi.*

Ethyl Bromide.

Hydrobromic ether, C_2H_5Br.—A colorless liquid; boils at 40.7°; has an ethereal odor; a taste at first sweet, afterward disagreeable and burning. Obtained by the combined action of phosphorus and bromine on ethylic alcohol. Possesses anæsthetic properties.

Ethyl Iodide.

Hydriodic ether, C_2H_5I.—This compound, which is of considerable commercial importance since the introduction of the aniline industry, and which has also rendered very valuable service in the laboratory, is prepared by placing thirty-five parts of absolute alcohol and seven parts of phosphorus in a vessel surrounded by a freezing mixture, and gradually adding thirty-two parts of iodine; when the action has ceased, the liquid is decanted, distilled over the water-bath, and the distillate washed and purified.

It is a colorless liquid; heavier than water; boils at 72.2°; has a powerful ethereal odor, and becomes brown when exposed to the light. It burns with difficulty.

Similarly constituted chlorides, bromides, and iodides of the higher radicals of this series have been obtained; they resemble those described in their properties and methods of formation. The use of amyl chloride, $C_5H_{11}Cl$, as an anæsthetic, has been suggested.

Products of Further Substitution.

When chlorine is allowed to act upon marsh-gas, it replaces one or more atoms of hydrogen, according to the proportions of the two gases and the energy of the reaction. If we consider marsh-gas as being the hydride of the radical methyl, the first of these products is the simple methyl chloride, already mentioned; the second, the chloride of a radical obtained from methyl by the substitution of one atom of chlorine for one of its atoms of hydrogen, CH_2Cl_2, etc. The formation of these products may be indicated thus:

$$CH_4+Cl_2=HCl+CH_3Cl.$$
$$CH_4+2Cl_2=2HCl+CH_2Cl_2.$$
$$CH_4+3Cl_2=3HCl+CHCl_3.$$
$$CH_4+4Cl_2=4HCl+CCl_4.$$

Considering them as derivatives of marsh-gas, methyl hydride, they should be called: $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}$ = Methyl hydride = marsh-gas. $\left.\begin{matrix}CH_3\\Cl\end{matrix}\right\}$ = Methyl chloride. $\left.\begin{matrix}CH_2Cl\\Cl\end{matrix}\right\}$ = Monochlormethyl chloride. $\left.\begin{matrix}CHCl_2\\Cl\end{matrix}\right\}$ = Dichlormethyl chloride = chloroform. $\left.\begin{matrix}CCl_3\\Cl\end{matrix}\right\}$ = Trichlormethyl chloride = tetrachloride of carbon.

Similar products are formed with bromine and iodine.

Monochlormethyl Chloride.

Methene chloride—Methylene chloride—Dichloromethane—CH_2Cl,Cl.—By some chemists considered as the chloride of a divalent radical, $(CH_2)''$ = methylene, whose existence, however, in this compound is problematical.

It is obtained by the action of chlorine upon methyl chloride, or by shaking an alcoholic solution of chloroform with powdered zinc and a little ammonium hydrate, the nascent hydrogen thus formed separating a portion of the chlorine as hydrochloric acid. In either case the product must be purified.

It is a colorless, oily liquid; boils at 40°—42°; sp. gr., 1.36; its odor is similar to that of chloroform. It is very slightly soluble in water, and is not inflammable.

Under the names *bichloride of methylene* and *chloromethyl*, it has been used as a substitute for chloroform in the production of anæsthesia, and the hope was entertained that it would prove the safer agent of the two—a hope which subsequent experience has not justified. In the three years following its introduction (1868–1871) four cases of death from its use were recorded.

Dichlormethyl Chloride.

Methenyl chloride—Formyl chloride—Chloroform—Chloroformum (U. S., Br.)—$CHCl_2Cl$.—This important compound was discovered in 1831, by Dr. Samuel Guthrie, of Sackett's Harbor, N. Y., and at about the same time by Liebig, in Germany, and by Soubeiran, in France.

It is obtained by heating to 40°, in a capacious still, thirty-five to forty litres of water, adding five kilos of recently slacked lime and ten kilos of chloride of lime; two and one-half litres of alcohol are then added, and the temperature is quickly raised until the product begins to distil over, when the fire is withdrawn, the action continuing of itself until toward the end, when heat is again applied. By this process, the crude chloroform of the dispensatory, *Chloroformum venale* (U. S.), is obtained. It is still very impure, and, to purify it, it is first shaken with sulphuric acid, from which it is separated by decantation, then thoroughly mixed with alcohol and recently ignited potassium carbonate, the mixture shaken, and redistilled at the temperature of the water-bath; the distillate is pure chloroform.

Chloroform is a colorless, volatile liquid, having a strong, agreeable ethereal odor, and a sweet taste. It is heavier than water (sp. gr. 1.497); very sparingly soluble in water; miscible with alcohol and ether in all proportions; boils at 60.8°. It ignites with difficulty, but may be burned from a cotton wick, giving a red, smoky flame, bordered with green, which gives off vapors of hydrochloric acid. It is a good solvent for many substances insoluble in water—phosphorus, iodine, fats, resins, caoutchouc, gutta-percha, and the alkaloids.

Chloroform is not acted on by concentrated sulphuric acid, except by long contact, when hydrochloric acid is given off. Chlorine, under the influence of direct sunlight, converts it into tetrachloride of carbon, CCl_4, and hydrochloric acid. It is not attacked by the alkalies in aqueous solution; but when heated with them in alcoholic solution, it is decomposed with formation of chloride and formiate of the alkaline metal. If a small quantity of aniline be present during the action of the alcoholic solution of the alkali upon chloroform, isobenzonitril is formed, and may be recognized by its peculiar odor. Perfectly pure chloroform is not altered by exposure to light; but if it contain compounds of nitrogen, even in very minute quantity (derived from impurities in the sulphuric acid used in its purification), it is gradually decomposed, when exposed to direct sunlight, into hydrochloric acid, chlorine, and other substances.

The most notable property of chloroform is its power of producing anæsthesia when its vapor, largely diluted with air, is inhaled. *If chloroform be used at all as an anæsthetic*, the physician should satisfy himself of its purity before using it. The substances with which it is liable to be contaminated are alcohol, aldehyde, hydrochloric acid, and methyl compounds. Alcohol may be detected, if present in large quantity, by the low specific gravity of the chloroform, by its sinking through water in opaque, pearly drops, and by the slow separation and diminution in volume of a measured quantity of chloroform when shaken with water. If alcohol be present in small quantity, it is revealed by the production of a green color when the impure chloroform is shaken with ferrous dinitrosulphide (obtained by acting on ferric chloride with a mixture of potassium nitrate and ammonium hydrosulphide). Chloroform containing aldehyde communicates a brown color to liquor potassæ heated with it.

Chloroform containing hydrochloric acid reddens blue litmus paper, and causes a white precipitate in an aqueous solution of silver nitrate, when shaken with it. Probably the most dangerous contaminations of chloroform are certain methylic and empyreumatic compounds, which, if improperly prepared, it contains in small quantities. The absence of these is ascertained by: 1st, shaking the chloroform, in a glass-stoppered bottle, with an equal volume of colorless sulphuric acid. After twenty-four hours the chloroform (upper) layer should be perfectly colorless, and the acid layer colorless or faintly tinged with yellow; 2d, evaporating a small quantity spontaneously, the last portions should have no pungent odor, and the remaining film of moisture should have no odor or taste other than those of chloroform.

Toxicology.—The action of chloroform varies as it is taken by the stomach or by inhalation. In the former case, owing to its insolubility, but little is absorbed, and the principal action is the local irritation of the mucous surfaces. Recovery has followed a dose of four ounces, and death has been caused by one drachm, taken into the stomach.

Chloroform vapor acts much more energetically, and seems to owe its potency for evil to its paralyzing influence upon the nerve-centres, notably upon those of the heart. While persons suffering from heart disease are particularly susceptible to the paralyzing effect of chloroform vapor, there are several cases recorded of death from the inhalation of small quantities, properly diluted, in which no heart-lesion was found upon a post-mortem examination.

Chloroform is apparently not altered in the system, and is eliminated with the expired air.

There is no chemical antidote to chloroform. When it has been swallowed, the stomach-pump and emetics are indicated; when taken by inhalation, a free circulation of air should be established about the face; artificial respiration and the application of the induced current to the sides of the neck should be resorted to.

The nature of the poison is usually revealed at the autopsy by its peculiar odor, which is most noticeable on opening the cranial and thoracic cavities. In a toxicological analysis, chloroform is to be sought for especially in the lungs and blood. These are placed in a flask, if acid, neutralized with sodium carbonate, and subjected to distillation at the temperature of the water-bath. The vapors are passed through a tube of difficultly fusible glass; at first the tube is heated to redness for about an inch of its length, and a piece of filter-paper, moistened with starch paste and with a solution of potassium iodide, is held at the orifice; if chloroform vapor be present, it is decomposed into carbon, hydrochloric acid, and free chlorine, and the last-named turns the paper blue by the liberation of iodine (the color is afterward bleached if chlorine be present in large quantity). The escaping vapor is then allowed to bubble through a solution of silver nitrate acidulated with nitric acid, when, if chloroform be present, a white precipitate, soluble in ammonia, is formed. Finally, the tube is allowed to cool, and the distillate collected in a pointed tube; if chloroform be present in considerable quantities it collects in a distinct layer or in drops at the lower, pointed end of the receiver. The supernatant, watery liquid is drawn off with a pipette; the drops of chloroform, whose odor may be recognized, dissolved in a small quantity of alcohol, and to this solution a little alcoholic solution of potassium hydrate and two or three drops of aniline are added, and the mixture gently warmed; if chloroform be present, even in small quantity (one part to five thou-

sand parts alcohol) the peculiar, disagreeable odor of isobenzonitril is observed (Hofmann).

Tetrachloride of Carbon, CCl_4—the product of the most complete substitution of chlorine for hydrogen in marsh-gas. It is formed by the prolonged action of chlorine upon methyl chloride, or upon chloroform, under the influence of direct sunlight. More quickly by passing chlorine, charged with vapor of carbon disulphide, through a red-hot tube, and purifying the product.

It is a colorless, oily liquid, insoluble in water, soluble in alcohol and in ether; having an agreeable ethereal odor; sp. gr. 1.56; boiling at 78°. Its vapor, when heated to redness, either alone or mixed with hydrogen, is decomposed, yielding a mixture of dichloride, C_2Cl_4, trichloride, C_2Cl_6, and free chlorine.

Its action upon the economy is similar to that of chloroform. It is known in pharmacy as *chlorocarbon.*

Dibromomethyl Bromide.

Methenyl bromide—Formyl bromide—Bromoform—$CHBr_3$, Br.—is prepared by gradually adding bromine to a cold solution of potassium hydrate, until the liquid begins to be colored, and rectifying over calcium chloride.

A colorless liquid of sp. gr. 2.13, having an aromatic odor and a sweet taste, less volatile than chloroform, boils at 150°—152°, solidifies at —9°, sparingly soluble in water, to which it communicates its taste and odor, soluble in alcohol and ether. When boiled with alcoholic potash, it undergoes a decomposition similar to that of chloroform. It burns with difficulty, and is decomposed at a red heat.

Its physiological action is similar to that of chloroform. It often exists as an impurity in commercial bromine, accompanied by *carbon tetrabromide,* CBr_4.

Diiodomethyl Iodide.

Methenyl iodide—Formyl iodide—Iodoform—CHI_3.—Formed, like chloroform and bromoform, by the combined action of potash and the halogen upon alcohol; it is also produced by the action of iodine upon a great number of organic substances, and is usually prepared by heating to 60°—80° a mixture of three parts alkaline carbonate, ten parts water, one part iodine and one part ethylic alcohol, and purifying the product by recrystallization from alcohol.

Iodoform differs widely from its chlorine and bromine congeners both in appearance and properties. It is a solid, crystallizing in yellow hexagonal plates, which melt at 115°—120°. It may be sublimed, a portion being decomposed. It is insoluble in water, acids, and alkaline solutions; soluble in alcohol, ether, carbon disulphide, and the fatty and essential oils; the solutions, when exposed to the light, undergo decomposition and assume a violet-red color. It has a sweet taste and a peculiar, penetrating odor, resembling, when the vapor is largely diluted with air, that of saffron. When heated with potash, a portion is decomposed into formiate and iodide, while another portion is carried off unaltered with the aqueous vapor. It contains 96.7% of its weight of iodine.

It possesses anæsthetic powers, less active than those of chloroform and bromoform, and principally localized to the sphincters. Experiments upon animals show that it is poisonous in smaller doses than iodine.

Dichlormethyl Iodide.

Chloroiodoform, $CHCl_2I$—is formed when iodoform is heated with mercuric chloride; a dark red liquid distils, which, when treated with potash and redistilled, yields a yellowish liquid, having an aromatic odor and a sweetish taste; sp. gr. 1.96.

Dibromomethyl Iodide.

Bromoiodoform, $CHBr_2I$—is a colorless liquid, solidifying at 0°, very volatile, sweet in taste, having a penetrating odor; obtained by the action of bromine upon iodoform.

Chlorinated Derivatives of Ethyl Chloride.

By the action of chlorine upon ethyl chloride, a progressive substitution of atoms of chlorine for atoms of hydrogen occurs, with formation of the following substances:

Monochlorethyl chloride	C_2H_4Cl,Cl	boils at 64°
Dichlorethyl chloride	$C_2H_3Cl_2,Cl$	boils at 75°
Trichlorethyl chloride	$C_2H_2Cl_3,Cl$	boils at 102°
Tetrachlorethyl chloride	C_2HCl_4,Cl	boils at 146°
Carbon trichloride	C_2Cl_6	boils at 182°

The first of these is isomeric with "Dutch liquid" (see page 229) and possesses anæsthetic powers. A product containing the three following, in varying quantities, has been used as an anæsthetic under the names *æther anæstheticus Arani*. *Carbon trichloride*, also called *sesquichloride* or *perchloride of carbon*, is obtained by the action of chlorine upon ethyl chloride or upon Dutch liquid, under the influence of sunlight. It forms colorless, transparent crystals, almost tasteless, having an odor resembling that of camphor; hard, insoluble in water, soluble in alcohol and in ether, fusing at 160°, volatile at 182°. Has been used medicinally as a local anæsthetic, and in cholera.

MONOATOMIC ALCOHOLS.

Series $C_nH_{2n+2}O$.

This series consists of the hydrates of the radicals C_nH_{2n+1}, derived from the saturated hydrocarbons (see pp. 149, 157), and contains some of the most important of the organic compounds. The following is a list of the terms of the series which have been studied, and their prominent physical properties.

ALCOHOLS—SERIES $C_nH_{2n+2}O$.

Name.	Empirical formula.	Typical formula.	Fusing-point.	Boiling-point.	Specific gravity.
Methyl hydrate	CH_4O	$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$	..	66°.5	0.814
Ethyl hydrate	C_2H_6O	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	..	78°.3	0.8095
Propyl hydrate	C_3H_8O	$\left.\begin{matrix}C_3H_7\\H\end{matrix}\right\}O$	..	96°.7	0.820
Butyl hydrate	$C_4H_{10}O$	$\left.\begin{matrix}C_4H_9\\H\end{matrix}\right\}O$	..	114°.7	0.817
Amyl hydrate	$C_5H_{12}O$	$\left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\}O$	20°	132°	....
Hexyl hydrate	$C_6H_{14}O$	$\left.\begin{matrix}C_6H_{13}\\H\end{matrix}\right\}O$	..	150°	0.820
Heptyl hydrate	$C_7H_{16}O$	$\left.\begin{matrix}C_7H_{15}\\H\end{matrix}\right\}O$	..	168°	....
Octyl hydrate	$C_8H_{18}O$	$\left.\begin{matrix}C_8H_{17}\\H\end{matrix}\right\}O$	..	186°	....
Nonyl hydrate	$C_9H_{20}O$	$\left.\begin{matrix}C_9H_{19}\\H\end{matrix}\right\}O$	..	204°	....
Decyl hydrate	$C_{10}H_{22}O$	$\left.\begin{matrix}C_{10}H_{21}\\H\end{matrix}\right\}O$	..	....	....
Cetyl hydrate	$C_{16}H_{34}O$	$\left.\begin{matrix}C_{16}H_{33}\\H\end{matrix}\right\}O$	49°	....	....
Ceryl hydrate	$C_{27}H_{56}O$	$\left.\begin{matrix}C_{27}H_{55}\\H\end{matrix}\right\}O$	79°	....	....
Myricyl hydrate	$C_{30}H_{62}O$	$\left.\begin{matrix}C_{30}H_{61}\\H\end{matrix}\right\}O$	85°	....	....

Methyl Hydrate.

Methylic alcohol—Carbinol—Pyroxylic spirit—Wood spirit—CH_3HO.—Does not exist in nature, may be obtained from marsh-gas, methyl hydride, by first converting it into the iodide, which is then acted upon by potassium hydrate:

$$CH_3I+KHO=KI+CH_3HO.$$

It is obtained in the arts by the destructive distillation of wood (whence the name, from *μέθυ*, wine, and *ὕλη*, wood). When wood is decomposed at a high temperature in closed vessels, there are formed charcoal, gaseous and tarry products, and an aqueous fluid which is known as *crude wood vinegar*, and contains a number of substances, notably acetic acid and methylic alcohol. The crude vinegar is separated by decantation from the tarry products and redistilled, the first tenth is collected, treated with quicklime and again distilled; the distillate treated with dilute sulphuric acid, decanted, and again distilled from quicklime; the product, still quite impure, is the *wood alcohol*, *wood naphtha*, and *pyroxylic spirit* of commerce. It may be further purified by causing it to combine with calcium chloride, decomposing the crystalline compound formed by the addition of water, and rectifying from quicklime; all these distillations are carried

on at the temperature of the water-bath. The pure hydrate is obtained by forming a crystalline compound, such as methyl oxalate, which is purified, decomposed, and the product rectified until the boiling-point is constant at 66.5°.

Pure methyl alcohol is a colorless liquid, having an ethereal and alcoholic odor, and a sharp, burning taste; sp. gr. 0.814 at 0°; boils at 66.5°, bumping so as to render its distillation difficult. It burns with a pale flame, giving less heat than that of ethylic alcohol. It mixes with water, alcohol, and ether in all proportions; is a good solvent of resinous substances, and also dissolves sulphur, phosphorus, potash, and soda, the solutions of the last-named substances becoming colored on contact with air.

Methyl hydrate is not affected by exposure to air under ordinary circumstances, but in the presence of platinum-black it is oxidized, with formation of the corresponding aldehyde and acid, formic acid.

Nitric acid, aided by heat, decomposes it with formation of nitrous fumes, formic acid, and methyl nitrate. When heated with nitric acid and silver nitrate, it produces no fulminate. Sulphuric acid acts upon methyl alcohol as it does upon ethyl hydrate (*q.v.*). The organic acids produce ethers with methyl alcohol, as they do with all the members of the series.

It dissolves potassium and sodium with liberation of hydrogen, and the formation of oxides of methyl and potassium or sodium; $\left.\begin{matrix}CH_3\\K\end{matrix}\right\}O$ or $\left.\begin{matrix}CH_3\\Na\end{matrix}\right\}O$. With baryta and with calcium chloride it forms crystallized compounds. With hydrochloric acid, under the influence of the galvanic current, it forms an oily substance having the composition C_2H_3ClO.

Uses.—It is used in the arts in the preparation of varnishes; as a solvent in many processes, and in the manufacture of aniline dyes.

Methylated spirit is ethyl alcohol containing sufficient wood spirit to render it unfit for the manufacture of ardent spirits by reason of the disgusting odor and taste which crude wood alcohol owes to certain empyreumatic products which it contains. Spirits so treated are not subject to the heavy duties imposed upon ordinary alcohol, and are, therefor, largely used in the arts and for the preservation of anatomical preparations; it contains one-ninth of its bulk of wood naphtha.

When taken internally it produces the same effects as does ordinary alcohol; it seems, however, to be rather more active. Its use as a therapeutic agent has been suggested.

Ethyl Hydrate.

Ethylic alcohol—Methyl carbinol—Vinic alcohol—Alcohol—Spirits of wine—C_2H_5HO.—Liquids containing alcohol were known and were prepared for use as beverages in remote antiquity. It was only in the middle ages, however, that the alchemists separated alcohol, still containing water, from wine, whence it received the name, still used in speaking of diluted alcohol, of spirits of wine. Saussure was the first to determine its composition.

Alcohol does not exist in nature, but is produced in a number of reactions. One method of its formation, which has an historical interest as

that by which its constitution was determined, is by the formation of sulphovinic acid and the subsequent decomposition of this by water:

$$\underset{\text{Sulphuric acid.}}{SO_4H_2} + \underset{\text{Ethylene}}{C_2H_4} = \underset{\text{Sulphovinic acid.}}{SO_4HC_2H_5}$$

$$\underset{\text{Sulphovinic acid.}}{SO_4HC_2H_5} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphuric acid.}}{SO_4H_2} + \underset{\text{Alcohol.}}{C_2H_5OH}$$

The sources from which alcohol and alcoholic liquids are industrially obtained are always vegetable substances, rich in starch or in glucose, by far the greater proportion being obtained from starchy materials.

The manufacture of alcohol from this source consists of three distinct processes: 1st, the conversion of starch into sugar; 2d, the fermentation of the saccharine liquid; 3d, the separation, by distillation, of the alcohol formed by fermentation.

The raw materials for the first process are *malt* and some substance (grain, potatoes, rice, corn, etc.) containing starch. Malt is barley which has been allowed to germinate, and, at the proper stage of germination, roasted. During this growth there is developed in the barley a peculiar nitrogenous principle called *diastase*. The starchy material is mixed with a suitable quantity of malt and water, and the mass maintained at a temperature of 65°—70° for two to three hours, during which the diastase rapidly converts the starch into *dextrine*, and this in turn into *glucose*. The saccharine fluid, or *wort*, obtained in the first process, is drawn off, cooled, and *yeast* is added. As a result of the growth of the yeast-plant, a complicated series of chemical changes take place, the principal one of which is the splitting up of the glucose into carbon dioxide and alcohol:

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = 2\underset{\text{Alcohol.}}{C_2H_5OH} + 2\underset{\text{Carbon dioxide.}}{CO_2}$$

There are formed at the same time small quantities of glycerine, succinic acid, and propyl, butyl, and amyl alcohols.

An aqueous fluid is thus obtained which contains from three to fifteen per cent. of alcohol; this is then separated by the third process, that of distillation or rectification. The apparatus used for this purpose has been so far perfected that by a single distillation an alcohol of 90—95 per cent. can be obtained.

In some cases alcohol is prepared from fluids rich in glucose, such as grape-juice, molasses, syrup, etc.; in such cases the first process becomes unnecessary.

Commercial alcohol always contains water, and when pure or *absolute* alcohol is required, the commercial product must be mixed with some hygroscopic solid substance, such as quicklime, from which it is distilled after having remained in contact twenty-four hours.

Alcohol is a thin, colorless, transparent liquid, having a spirituous odor, and a sharp, burning taste; sp. gr. 0.8095 at 0°, 0.7939 at 15°; it boils at 78.5°, and has not been solidified; at temperatures below —90° it is viscous. It mixes with water in all proportions, the union being attended by elevation in temperature and contraction in volume (after cooling to the original temperature). If 52.3 volumes of alcohol be mixed with 47.07 of water, at 15°, the mixture occupies 96.35 volumes, the maximum of

contraction. It also attracts moisture from the air to such a degree that absolute alcohol only remains such for a very short time after its preparation. It is to this power of attracting water that alcohol owes its preservative power for animal substances, and probably also its power of coagulating albuminoid substances. It is a very useful solvent, dissolving a number of gases, most of the mineral and organic acids and alkalies, most of the chlorides and carbonates, some of the nitrates, all the sulphates, essences, and resins. Most of the varnishes consist of alcoholic solutions of resinous materials. Alcoholic solutions of fixed medicinal substances are called *tinctures;* those of volatile principles, *spirits.*

The action of oxygen upon alcohol varies according to the conditions. Under the influence of energetic oxidants, such as chromic acid, or, when alcohol is burned in the air, the oxidation is rapid and complete, and is attended by the extrication of much heat and the formation of carbon dioxide and water:

$$C_2H_6O+3O_2=2CO_2+3H_2O.$$

Mixtures of air and vapor of alcohol explode upon contact with flame. If a less active oxidant be used, such as platinum-black, or by the action of atmospheric oxygen at low temperatures, a simple oxidation of the alcoholic radical takes place, with formation of acetic acid:

$$\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O+O_2=\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O+H_2O,$$

a reaction which is utilized in the manufacture of acetic acid and vinegar. If the oxidation be still further limited, *aldehyde* is formed:

$$2C_2H_6O+O_2=2C_2H_4O+2H_2O.$$

If vapor of alcohol be passed through a tube filled with platinum sponge and heated to redness, or if a coil of heated platinum wire be introduced into an atmosphere of alcohol vapor, the products of oxidation are quite numerous; among them are water, ethylene, aldehyde, acetylene, carbon monoxide, and acetal. Heated platinum wire introduced into vapor of alcohol continues to glow by the heat resulting from the oxidation, a fact which has been utilized in Doebereiner's flameless lamp, and in the thermocautery recently introduced in surgical practice.

Chlorine and bromine act energetically upon alcohol, producing a number of chlorinated and brominated derivatives, the final products being *chloral* and *bromal* (*q. v.*). If the action of chlorine be moderated, aldehyde and hydrochloric acid are first produced. Iodine acts quite slowly in the cold, but old solutions of iodine in alcohol (tr. iodine) are found to contain hydriodic acid, ethyl iodide, and other imperfectly studied products. In the presence of an alkali, iodine acts upon alcohol to produce iodoform.

Potassium and sodium dissolve in alcohol with evolution of hydrogen; upon cooling, a white solid crystallizes, which is the double oxide of ethyl and the alkaline metal:

$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}K\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}O$
Water or hydrogen oxide.	Potassium hydrate or oxide of hydrogen and potassium.	Ethyl hydrate or oxide of hydrogen and ethyl.	Oxide of ethyl and potassium.

These compounds, on contact with water, are decomposed, with regeneration of alcohol and formation of the alkaline hydrate.

Nitric acid, aided by a gentle heat, acts violently upon alcohol, producing nitrous ether, brown fumes, and products of oxidation. For the action of other acids upon alcohol see the corresponding ethers.

The hydrates of the alkaline metals dissolve in alcohol, but react upon it slowly; the solution turns brown and contains an acetate.

If alcohol be gently heated with nitric acid and the nitrate of silver or of mercury, a gray precipitate falls, which is silver or mercury fulminate.

Uses.—Alcohol is used in a great number of processes, in the arts, and in pharmacy, principally as a solvent, but also as a starting-point in the manufacture of a number of substances, as vinegar, chloral, chloroform, and ether; as a menstruum in the preparation of tinctures and spirits; and to a certain extent as a fuel, when a hot and smokeless flame is desired.

It occurs in commerce, and is used pharmaceutically in different degrees of concentration.

Absolute alcohol is pure alcohol, C_2H_6O, prepared as desired by the method given above. It is not purchasable; the so-called absolute alcohol of the shops is rarely stronger than ninety-eight per cent.

Alcohol fortius (U. S.)—stronger alcohol, is of sp. gr. 0.817, and contains ninety-two per cent. alcohol.

Alcohol (U. S.)—sp. gr. 0.835 = *Spiritus rectificatus* (Br.)—sp. gr. 0.838—is the ordinary rectified spirit, used for most purposes in the arts; it contains eighty-five per cent. alcohol.

Alcohol dilutum (U. S.)—sp. gr. 0.941 = *Spiritus tenuior* (Br.)—sp. gr. 0.920—used for the preparation of tinctures. It contains thirty-nine per cent., U. S., or forty-nine per cent., Br., of alcohol. The British officinal is of the same strength as the *proof spirit* of commerce.

Physiological action.—In a concentrated form, alcohol exerts a dehydrating action upon animal tissues with which it comes in contact; causing coagulation of the albuminoid constituents. When diluted, ethylic alcohol may be a food, a medicine, or a poison, according to the dose and the condition of the person taking it. When taken in excessive doses, or in large doses for a long time, it produces the symptoms and lesions characteristic of pure alcoholism, acute or chronic, modified or aggravated by those produced by other substances, such as amyl alcohol, which accompany it in the alcoholic fluids used as beverages. Taken in moderate quantities, with food, it aids digestion and produces a sense of comfort and exhilaration. As a medicine it is the most valuable of stimulants.

Much has been written concerning the value of alcohol as a food. If it have any value as such, it is as a producer of heat and force by its oxidation in the body; experiments made in the interest of teetotalism have failed to show that more than a small percentage (sixteen per cent. in twenty-four hours) of medium doses of alcohol ingested are eliminated by all channels; the remainder, therefor, disappears in the body, as the idea that it can there "accumulate" is entirely untenable. That some part should be eliminated unchanged is to be expected from the rapid diffusion and the high volatility of alcohol.

On the other hand, if alcohol be oxidized in the body, we should expect, in the absence of violent muscular exercise, an increase in temperature, and the appearance in the excreta of some product of oxidation of alcohol, aldehyde, acetic acid, carbon dioxide, or water, while the elimi-

nation of nitrogenous excreta, urea, etc., would remain unaltered or be diminished. While there is no doubt that excessive doses of alcohol produce a diminution of body temperature, the experimental evidence concerning the action in this direction of moderate doses is conflicting and incomplete.

Of the products of oxidation, aldehyde has not been detected in the excreta, and acetic acid only in the intestinal canal. The elimination of carbonic acid, as such, does not seem to be increased, although positive information upon this point is wanting. If acetic acid be produced, this would form an acetate, which in turn would be oxidized to a carbonate, and eliminated as such by the urine. The elimination of water under the influence of large doses of alcohol is greater than at other times, but whether this water is produced by the oxidation of the hydrogen of the alcohol, or is removed from the tissues by its dehydrating action, is an open question.

While physiological experiment yields only uncertain evidence, the experience of arctic travellers and others shows that the use of alcohol tends to diminish rather than increase the capacity to withstand cold. The experience of athletes and of military commanders is that intense and prolonged muscular exertion can be best performed without the use of alcohol. The experience of most literary men is that long-continued mental activity is more difficult with than without alcohol.

In cases of acute poisoning by alcohol, the stomach-pump and catheter should be used as early as possible. A plentiful supply of air, the cold douche, and strong coffee are indicated.

Analysis.—The presence of alcohol may be detected by the following reactions, none of which, taken alone, is, however, characteristic of alcohol under all circumstances.

First.—If a solution containing alcohol be heated with a small quantity of solution of potassium dichromate and sulphuric acid, the liquid assumes an emerald green color, and, if the quantity of alcohol be not too small, the peculiar fruity odor of aldehyde is observed. The green color is produced under like circumstances by many reducing agents.

Second.—If an alcoholic liquid be warmed and treated with a few drops of potassium hydrate solution and a small quantity of iodine, a yellow, crystalline precipitate of iodoform is produced, either immediately or after a time. Many other organic substances produce iodoform under similar conditions.

Third.—If nitric acid be added to a liquid containing alcohol, nitrous ether, recognizable by its odor, is given off; if a solution of mercurous nitrate with excess of acid be then added, and the mixture heated, a further evolution of nitrous ether occurs, and a yellowish-gray deposit of fulminating mercury is formed, which may be collected, washed, dried, and exploded. This reaction is well adapted to detecting ethylic in methylic alcohol, as the latter does not form a fulminate.

Fourth.—Alcohol may be detected in chloroform by shaking it with a fragment of dry potassium hydrate, removing the potash, and shaking the chloroform with an equal volume of solution of cupric sulphate; a blue precipitate is formed if the chloroform contained alcohol.

Fifth.—If an alcoholic liquid be heated for a few moments with sulphuric acid, diluted with water and distilled, the distillate, on treatment with sulphuric acid and potassium permanganate, and afterward with sodium hyposulphite, yields aldehyde, which may be recognized by the production of a violet color on the addition of a dilute solution of fuchsine.

The *quantity* of alcohol in an alcoholic liquid is usually determined by observing the specific gravity. If the liquid contain a large quantity of alcohol and little or no solid matter, as in the case of the alcohols of commerce, this is done directly; if, however, the liquid hold solid matters in solution, as in the case of wines and spirits containing sugar, a measured volume of the liquid is distilled until the alcohol is all driven into the distillate, whose specific gravity is then determined. The following table indicates the percentage of alcohol in mixtures of water and alcohol of different specific gravity, at 60° F.=15.5° C.:

Alcohol per cent.	Specific gravity.	Alcohol per cent.	Specific gravity.	Alcohol per cent.	Specific gravity.	Alcohol per cent.	Specific gravity.
0	1.0000	25	0.9652	51	0.9160	76	0.8581
0.5	9991	26	9638	52	9135	77	8557
1	9981	27	9623	53	9113	78	8533
2	9965	28	9609	54	9090	79	8508
3	9947	29	9593	55	9069	80	8483
4	9930	30	9578	56	9047	81	8459
5	9914	31	9560	57	9025	82	8434
6	9898	32	9544	58	9001	83	8408
7	9884	33	9528	59	8979	84	8382
8	9869	34	9511	60	8956	85	8357
9	9855	35	9490	61	8932	86	8331
10	9841	36	9470	62	8908	87	8305
11	9828	37	9452	63	8886	88	8279
12	9815	38	9434	64	8863	89	8254
13	9802	39	9416	65	8840	90	8228
14	9789	40	9396	66	8816	91	8199
15	9778	41	9376	67	8793	92	8172
16	9766	42	9356	68	8769	93	8145
17	9753	43	9335	69	8745	94	8118
18	9741	44	9314	70	8721	95	8089
19	9728	45	9292	71	8696	96	8061
20	9716	46	9270	72	8672	97	8031
21	9704	47	9249	73	8649	98	8001
22	9691	48	9228	74	8625	99	7969
23	9678	49	9206	75	8603	100	7938
24	9665	50	9184				

Alcoholic Beverages.

The variety of beverages in whose preparation alcoholic fermentation plays an important part is very great, and the products differ from each other materially in their composition and in their physiological action. They may be divided into four classes, the classification being based upon the sources from which they are obtained and upon the method of their preparation.

I.—Those prepared by the fermentation of malted grain—*beers, ales, and porters.*

II.—Those prepared by the fermentation of grape-juice—*wines.*

III.—Those prepared by the fermentation of the juices of fruits other than the grape—*cider, fruit-wines.*

IV.—Those prepared by the distillation of some fermented saccharine liquid—*ardent spirits.*

Beer, ale, and porter are aqueous infusions or decoctions of malted grain (occasionally of rice, maize, or potatoes), fermented and flavored with hops; they contain, therefor, the soluble constituents of the grain employed; dextrine and glucose, produced during the malting; alcohol and carbon dioxide produced during the fermentation; and the soluble constituents of the flavoring material. Their color, which varies from pale amber to dark brown, depends upon the proportion of malt, dried at a high temperature, used in their preparation.

The alcoholic strength of malt liquors varies from 1.5 to 9 per cent. Weiss bier contains 1.5—1.9 per cent.; lager, 4.1—4.5 per cent.; bock bier, 3.88—5.23 per cent.; London porter, 5.4—6.9 per cent.; Burton ale, 5.9 per cent.; Scotch ale, 8.5—9 per cent. Malt liquors all contain a considerable quantity of nitrogenous material (0.4—1 per cent. N.), and succinic, lactic, and acetic acids. The amount of inorganic material, in which the phosphates of potassium, sodium, and magnesium predominate largely, varies from 0.2 to 0.3 per cent. The amount of water varies from 79.66 in Burton ale, to 91.8 in weiss bier. The specific gravity from 1.014 to 1.033.

The adulterations of malt liquors are numerous and varied. Water is added to increase bulk; it may be detected by the taste, and by the low specific gravity of the beer deprived of its alcohol. Sodium carbonate is frequently added with the double purpose of neutralizing an excess of acetic acid and increasing the foam. The most serious adulteration of beer consists, however, in the introduction of bitter principles other than hops, and notably of strychnine, cocculus indicus (picrotoxin), and picric acid. Of late years artificial glucose (made from starch by the action of dilute sulphuric acid) has been used by some brewers; a substitution which would be perfectly justifiable and harmless, were it not for the fact that glucose prepared in this way is frequently, if not always, contaminated with arsenic, which it derives from the acid used in its manufacture.

Wines have been in use from remote antiquity, and are prepared in infinite variety in almost all temperate countries.

The grapes are collected with more or less care, and in different degrees of ripeness; for the finest grades each berry is separately plucked as it reaches the proper degree of ripeness; for the commonest ripe, unripe, and damaged grapes are thrown into the press indiscriminately. In the manufacture of most red wines and of champagnes, the grape is not allowed to reach full maturity. The grapes are expressed, and the juice, together with the skins and seeds, or *marc*, is placed in a butt with a perforated bottom, through which it is allowed to trickle into the fermentation vats; in the case of red wines the marc is allowed to remain in contact with the *must*, or juice, during a part at least of the fermentation, in order that the alcohol developed may take up a proper quantity of coloring matter; in the case of white wines, contact with a small quantity of the stalks is necessary to avoid *stringiness*. The fermentation of the must, which takes place without the addition of yeast, requires about fourteen days, at the end of which the wine is drawn off from the lees into barrels, in which it is kept at a low temperature, and protected from the air as far as possible, to avoid the establisment of acetic fermentation. If the must be rich in glucose and poor in nitrogenized material, and if the fermentation be arrested before the glucose has been entirely converted into alcohol, a sweet wine is obtained; under the contrary conditions a *dry* wine is the result. During the fermentation, as the percentage of alcohol increases, acid potassium tartrate is deposited, being insoluble in alcoholic liquids. Tartaric acid is the predominating acid in

the grape; while in other fruits malic and citric acids, whose acid salts are soluble in alcoholic liquids, exist in greater proportions; hence, the fermented drinks prepared from fruit other than grapes are sharp and thin in taste.

Most wines of good quality improve in flavor with age, and this improvement is greatly hastened by the process of *pasteuring*, which consists simply in warming the wine to a temperature of 60° C., without contact of air.

Wines grown in different districts, and from different kinds of grapes, differ greatly in their appearance, flavor, color, and alcoholic strength; they may be divided into two classes—*light* and *heavy* wines.

Light wines are those whose percentage of alcohol is less than twelve per cent. In this class are included the red and white French and German wines, clarets, Sauternes, Rhine, and Moselle wines; champagnes, Burgundies, the American wines, except some varieties of California wine, Australian, Greek, Hungarian, and Italian wines.

The champagnes and some Moselle wines are sparkling, a quality which is communicated to them by bottling them before the fermentation is completed, thus retaining the carbon dioxide, which is dissolved by virtue of the pressure which it exerts. They are dry and sweet in proportion as the sugar is completely or partially consumed during the fermentation. When properly prepared they are agreeable to the palate, and assist the digestion; when new, however, they are liable to communicate their fermentation to the contents of the stomach and thus seriously disturb digestion.

Of the still wines, the most widely used are the *clarets*, or red Bordeaux wines, and the *hocks*, or white Rhine and Moselle wines. The former are of low alcoholic strength, mildly astringent, and contain but a small quantity of nitrogenous material, qualities which render them particularly adapted to table use and as mild stimulants, especially for those predisposed to gout. The Rhine wines are thinner and more acid, and generally of lower alcoholic strength than the clarets. The Burgundy and Rhone wines are celebrated for their high flavor and body; they are not strongly alcoholic, but contain a large quantity of nitrogenous material, to which they are indebted for their notoriety as developers of gout.

Our native American wines, particularly those of the Ohio valley and of California, are yearly improving in flavor and quality; they more closely resemble the Rhine wines and Sauternes than other European wines.

Heavy wines are those whose alcoholic strength is greater than twelve per cent, usually fourteen to seventeen per cent; they include the sherries, ports, Madeiras, Marsala, and some California wines, and are all the products of warm climates.

Sherry is an amber-colored wine, grown in the south of Spain, and officinal under the name of *Vinum Xericum* (U. S., Br.). Marsala closely resembles sherry in appearance, and is frequently substituted for it. Port, officinal as *Vinum portense* (U. S.), is a rich, dark red wine, grown in Portugal.

The adulteration of wine by the addition of *foreign* substances is confined almost entirely to their artificial coloration, which is produced by the most various substances, indigo, logwood, fuchsine, etc. (see Bull. d. l. Soc. Chim. xxv., 435, 483, 530). The addition of natural constituents of wines, obtained from other sources, and the mixing of different grades of wine are, however, extensively practised. Water and

alcohol are the chief substances so added; an excess of the former may be detected by the taste, and the low specific gravity after expulsion of the alcohol. Most wines intended for export are *fortified* by the addition of alcohol; when the alcoholic spirit used is free from amyl alcohol, and is added in moderate quantities, there can be no serious objection to the practice, especially when applied to certain wines which, without such treatment, do not bear transportation. The mixing of fine grades of wine with those of a poorer quality is extensively practised, particularly with champagnes, clarets, and burgundies, and is perfectly legitimate. The same cannot be said, however, of the manufacture of factitious wine, either entirely from materials not produced from the grape, or by converting white into red wines, or by mixing wines with coloring matters, alcohol, etc., to produce imitations of wines of a different class, an industry which flourishes extensively in Normandy, at Bingen on the Rhine, and at Hamburg. The wines so produced are usually heavy wines, port and sherry, so-called.

In the following table are given, in percentages by weight, the chief constituents of the more generally used varieties of wine:

	Specific gravity.	Alcohol by weight.	Fixed acid, tartaric.	Volatile acid, acetic.	Total acid as tartaric.	Grape sugar.	Extractives.	Ash.	Tannin.
Claret	999.8	10.44	.374	.137	.580	2.255	1.64	.223	.18
Sauterne	992.2	10.84	.435	.169	.634	.088	1.82	.197	.18
Pomard	992.2	10.73	.435	.169	.634	.088	1.82	.197	.18
Chablis	992.2	7.77	.435	.169	.634	.088	1.46	.197	.18
Rhine wine	993.5	9.98	.440	.217	.538	.310	1.25	.182	.18
Hungarian, red	992.5	10.81	.386	.191	.628	.310	1.25	.122	.18
Hungarian, white	991.6	10.23	.419	.179	.644	.310	1·25	.047	.18
Sherry	992.9	17.89	.390	.055	.458	2.043	....	.437	.18
Sherry, dry	988.0	16.98	.379	.045	.435	.934	....	.567	.18
Sherry, imitation	996.0	16.48	.257	.111	.397	2.23	....	.327	.18
Madeira	1001.3	16.12	.528	.071	.610	3.0	4.02	.345	.18
Marsala	999.5	16.38	.241	.117	.389	.275	3.94	.311	.026
Port	992.2	12.08	.556	.048	.616	.669	4.49	.247	.026
Malaga	1057.0	12.04	.556	.048	.616	14.62	18.5	.38	.026
Tokay	1088.0	12.04	.556	.048	.616	14.62	1.06	.38	.026
Norton's Virginia	1038.0	9.53	.556	.048	.616	14.62	2.74	.38	.026
Catawba	1038.0	9.61	.556	.048	.616	14.62	1.7	.38	.026

Cider is the fermented juice of the apple, prepared very much in the same way as wine is from grape-juice and containing 3.5 to 7.5 per cent. of alcohol. It is very prone to acetous fermentation, which renders it sour and not only unpalatable, but liable to produce colic and diarrhœa with those not hardened to its use.

Spirits are alcoholic beverages, prepared by fermentation and distillation. They differ from beers and wines in containing a greater proportion of alcohol, and in not containing any of the non-volatile constituents of the grains or fruits from which they are prepared. Besides alcohol and water they contain acetic, butyric, valerianic and œnanthic ethers, to which they owe their flavor; sometimes tannin and coloring matter derived from the cask; amylic alcohol remaining after imperfect purifica-

tion; sugar intentionally added; and caramel. It is to the last-named substance that all dark spirits owe their color; although, after long keeping in wood a naturally colorless spirit assumes a straw color.

The varieties of spirituous beverages in common use are:

Brandy, spiritus vini gallici (U. S., Br.), obtained by the distillation of wine, and manufactured in France and in California and Ohio. It is of sp. gr. 0.929 to 0.934, is dark or light in color, according to the quantity of burnt sugar added, and contains about 1.2 per cent. of solid matter, of which 0.05 to 0.2 per cent. is ash. An inferior grade of brandy is prepared in wine-growing countries from the *marc*, or mass of grape-pulp, etc., left in the wine-press.

American whiskey, spiritus frumenti (U. S.), prepared from wheat, rye, barley, or Indian corn; has a specific gravity of 0.922 to 0.937 and contains 0.1 to 0.3 per cent. of solids. Its color is due partly to coloring matter from the wood of the cask, but mainly to added caramel.

Scotch and Irish whiskies, colorless spirits distilled from fermented grains; sp. gr. 0.915 to 0.920, having a peculiar smoky flavor produced by drying the malted grain by a peat fire.

Gin, also distilled from malted grain, sp. gr. 0.930 to 0.944, flavored with juniper and sometimes fraudulently with turpentine.

Rum.—A spirit distilled from molasses, and varying in color and flavor from the dark *Jamaica rum* to the colorless *St. Croix rum.* The former is of sp. gr. 0.914 to 0.926, and contains one per cent. of solid matter, of which 0.1 per cent. of ash.

Liqueurs are spirits sweetened and flavored with vegetable aromatics, and frequently colored; *anisette* is flavored with aniseed; *absinthe*, with wormwood; *curaçoa*, with orange-peel; *kirschwasser*, with cherries, the stones being cracked and the spirits distilled from the bruised fermented fruit; *kümmel*, with cummin and caraway seeds; *maraschino*, with cherries; *noyeau*, with peach and apricot kernels.

Propyl Hydrate.

Primary propyl alcohol—Ethyl carbinol—C_3H_7OH—is produced, along with ethylic alcohol, during fermentation, and obtained by fractional distillation of marc brandy, from *cognac oil, huilede marc* (not to be confounded with oil of wine), an oily matter, possessing to a high degree the flavor of brandy, which separates from marc brandy, distilled at high temperatures; and from the residues of manufacture of alcohol from beet-root, grain, molasses, etc. It is a colorless liquid, has a hot alcoholic taste, and a fruity odor; it boils at 96.7°; and is miscible with water. It has not been put to any use in the arts. Its intoxicating and poisonous actions are greater than those of ethyl alcohol. It exists in small quantity in cider.

There exists a *secondary propyl alcohol*, or *isopropyl alcohol* or *dimethyl carbinol*—$CH(CH_3)_2HO$—which is formed by the action of nascent hydrogen upon acetone; it boils at 86°.

Butyl Alcohols—C_4H_9OH.

Theoretically there are four possible butyl alcohols; two primary, one secondary, and one tertiary; of these three have been obtained:

Primary, normal butyl alcohol—Butyl alcohol of fermentation—Pro-

pyl carbinol—$CH_3—CH_2—CH_2—CH_2OH$—is formed in small quantities during alcoholic fermentation, and may be obtained by repeated fractional distillation from the oily liquid left in the rectification of vinic alcohol. It is a colorless liquid; boils at 114.7°; soluble in 10 parts water, from which it separates on the addition of a salt soluble in water. It is more actively poisonous than ethyl or methyl alcohol.

Secondary butyl alcohol; ethyl-methyl carbinol—$CH_3—\begin{matrix}CH_2\\CH_3\end{matrix}\!\!>\!CHOH$—a liquid which boils at 99°.

Tertiary butyl alcohol; trimethyl carbinol, $\begin{matrix}CH_3\\CH_3—COH\\CH_3\end{matrix}$—a crystalline solid, which fuses at 20°—25°, and boils at 82°.

Amylic Alcohols—$C_5H_{11}OH$.

Of the eight amylic alcohols whose existence theoretical considerations point out as possible (see p. 152), seven have been separated. The substance usually known as **amylic alcohol**, *potato spirit, fusel oil, alcohol amylicum* (U.S., Br.), is a mixture in varying proportions of the two primary alcohols; $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH—CH_2—CH_2OH$ and $\begin{matrix}CH_3—CH_2\\CH_3\end{matrix}\!\!>\!CH—CH_2OH$; the former differing from the latter in that it deviates the plane of polarization to the left ($[a]=-4°\ 36''$); in its boiling-point being 2° lower, and in the greater solubility of the amyl-sulphate of barium obtained from it.

It is formed during alcoholic fermentation of glucose in greater abundance than any of the alcohols other than the ethylic; owing to its high boiling-point, it is in great part retained in the oily material which collects in the still during the rectification of alcohol and spirits; a portion, however, passes over and is removed by subsequent treatment (see below).

It is obtained from the last milky products of rectification of alcoholic fluids made from grain or potatoes; these are shaken with water to remove ethyl alcohol, the supernatant oily fluid is decanted, dried by contact with fused calcium chloride, and distilled; that portion which passes over between 128° and 132° being collected.

It is a colorless, oily liquid, has an acrid taste and a peculiar odor, at first not unpleasant, afterward nauseating and provocative of severe headache; it boils at 132° and crystallizes at −20°; sp. gr. 0.8184 at 15°; it mixes with alcohol and ether, but not with water. It burns difficultly with a pale blue flame.

When exposed to air it oxidizes very slowly; quite rapidly, however, in contact with platinum-black, forming valerianic acid. The same acid, along with other substances, is produced, by the action of the more powerful oxidants upon amyl alcohol.

Chlorine attacks it energetically, forming amyl chloride, hydrochloric acid, and other chlorinated derivatives. Sulphuric acid dissolves in amyl alcohol, with formation of amyl-sulphuric acid, $SO_4(C_5H_{11})H$, corresponding to ethyl-sulphuric acid. It also forms similar acids with phosphoric, oxalic, citric, and tartaric acids.

Although not fragrant itself, its ethers, when dissolved in ethyl alcohol, have the taste and odor of various fruits, and are used in the preparation of artificial fruit-essences. Amyl alcohol is also used in analysis as a solvent, particularly for certain alkaloids, and in pharmacy for the artificial production of valerianic acid and the valerianates.

Its vapor, when inhaled, produces severe headache, a sense of suffocation, giddiness, and, in large doses, death. The liquid, taken internally, especially when in alcoholic solution, is much more actively poisonous than ethylic alcohol. Even in very dilute solution it produces the rapid intoxication, and severe headache and vertigo, which are prominent effects of inferior whiskey.

To free spirits of amyl alcohol, to *defuselate* them, advantage is usually taken of the absorbent power of freshly burnt wood charcoal, which is either placed in the still or made into a filter, through which the spirit is passed after distillation, or, preferably, the vapor from the still is made to pass through a layer of charcoal before condensation.

Spirits properly freed of fusel oil give off no irritating or foul fumes when hot; they are not colored red when mixed with three parts ethyl alcohol and one part strong sulphuric acid; they are not colored red or black by ammoniacal silver nitrate solution; when one hundred and fifty parts of the spirit mixed with one part potash, dissolved in a little water, are evaporated down to fifteen parts, and mixed with an equal volume of dilute sulphuric acid, no offensive odor should be given off.

No practical interest attaches to the alcohols of this series intermediate between amyl alcohol and

Cetyl Hydrate.

Cetylic alcohol—Ethal—$C_{16}H_{33}OH$—is obtained by the saponification of spermaceti (its palmitic ether) by potash. It is a white, crystalline solid, fusible at 49°, and capable of distillation at a high temperature; insoluble in water; soluble in alcohol and ether; tasteless and odorless.

Ceryl hydrate—$C_{27}H_{55}OH$—*cerylic* or *cerotic alcohol*, and **Myricyl hydrate**—$C_{31}H_{63}OH$—*myricic* or *mellissic alcohol*—are obtained as white, crystalline solids: the former from China wax; the second from beeswax, by saponification by potash.

SIMPLE ETHERS.

OXIDES OF ALCOHOLIC RADICALS OF THE SERIES C_nH_{2n+1}.

Methyl Oxide.

Methylic ether, $C_2H_6O-\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$—isomeric with ethylic alcohol, is obtained by the action of sulphuric and boric acids upon methyl alcohol, or by the action of silver oxide upon methyl iodide.

It is a colorless gas, has an ethereal odor, burns with a pale flame, liquefies at −36°, and distils at −21°; is soluble in water, ethyl alcohol, and sulphuric acid, less abundantly in methyl alcohol.

Ethyl Oxide.

Ethylic ether—Ether—Sulphuric ether—Æther fortior (U. S.)—*Æther purus* (Br.)—$C_4H_{10}O-\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$—was discovered in the sixteenth century by Val. Cordus, who called it *oleum vini dulce.*

It is obtained by the action of sulphuric acid upon alcohol, whence the name of "sulphuric ether" is improperly given it. A mixture is made of five parts alcohol, ninety per cent., and nine parts of concentrated sulphuric acid, in a vessel surrounded by cold water. This mixture is introduced into a retort, over which is conveniently arranged a vessel from which a slow stream of alcohol can be made to enter the retort. Heat is applied by a sand-bath, and the addition of alcohol is so regulated that the temperature does not rise above 140°. The retort is connected with a well-cooled condenser, and the process continued until the temperature in the retort rises above the point indicated. It is important that the tube by which the alcohol is introduced be drawn out to a small opening, and dip well down below the surface of the liquid. The distillate thus obtained contains, besides ether, alcohol, water, and gases resulting from the decomposition of the alcohol and sulphuric acid, notably sulphur dioxide. It is subjected to a first purification by shaking with water containing potash or lime, decanting the supernatant ether, and redistilling. The product of this process is "washed ether" or "æther, U. S." It is still contaminated with water and alcohol, and when desired pure, as for producing anæsthesia and for processes of analysis, it is subjected to a second purification. It is again shaken with water, decanted after separation, shaken with recently fused calcium chloride and newly burnt lime, with which it is left in contact twenty-four hours, and from which it is then distilled.

It was known at an early day that a small quantity of sulphuric acid is capable of converting a large quantity of alcohol into ether, and that at the end of the process the sulphuric acid remains in the retort unaltered, except by secondary reactions. A metaphysical explanation of the process was found in the assertion that the acid acted by its mere presence, by *catalysis*, as it was said; in other words, it acted because it acted, a very ready but a very feminine method of explaining what is not understood, which, we are sorry to say, is still invoked by some authors as a covering for our ignorance of the rationale of certain chemico-physiological phenomena.

It was only in 1850 that Alex. Williamson, by a series of ingenious and carefully conducted experiments, determined the true nature of the process. In the conversion of alcohol into ether, an intermediate substance, sulphovinic acid, plays an important part, being alternately formed at the expense of the alcohol, and destroyed with formation of ether and regeneration of sulphuric acid. At first sulphuric acid and alcohol act upon each other, molecule for molecule, to form water and sulphovinic acid:

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}SO_2\\C_2H_5\\H\end{matrix}\right\}O_2$$

The new acid, as soon as formed, reacts with a second molecule of alcohol, with regeneration of sulphuric acid and formation of ether:

$$\left.\begin{matrix}SO_2\\C_2H_5\\H\end{matrix}\right\}O_2 + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \left.\begin{matrix}SO_2\\H\end{matrix}\right\}O_2 + \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$$

Theoretically, therefor, a given quantity of sulphuric acid could convert an unlimited amount of alcohol into ether; such would also be the case in practice, were it not that the acid gradually becomes too dilute, by admixture with the water formed during the reaction, and at the same time is decomposed by secondary reactions, into which it enters with impurities in the alcohol; causes which in practice limit the amount of ether produced to about four to five times the bulk of acid used.

Properties.—Ether is a colorless, limpid, mobile, highly refracting liquid; it has a sharp, burning taste, and a peculiar, tenacious odor, characterized as ethereal. Sp. gr. 0.723 at 12.5°, and 0.7364 at 0°; it boils at 34.5°, and crystallizes at —31°. Its tension of vapor is very great, especially at high temperatures; it should, therefor, be stored in strong bottles, and should be kept in situations protected from elevations of temperature. It is exceedingly volatile, and, when allowed to evaporate freely, absorbs a great amount of heat, of which property advantage is taken to produce local anæsthesia, the part being benumbed by the cold produced by the rapid evaporation of ether sprayed upon the surface. Water dissolves one-ninetieth its weight of ether, and ether dissolves one thirty-sixth its weight of water. Ethylic and methylic alcohols are miscible with it in all proportions. Ether is an excellent solvent of many substances not soluble in water and alcohol, while, on the other hand, it does not dissolve many substances soluble in those fluids, properties which are of great value in proximate organic analysis. The resins and fats are readily soluble in ether; the salts of the alkaloids and many vegetable coloring matters are soluble in alcohol and water, but insoluble in ether, while the free alkaloids are for the most part soluble in ether, but insoluble, or very sparingly soluble, in water.

Ether, whether in the form of vapor or of liquid, is highly inflammable; the liquid burns with a luminous flame. The vapor forms with air a violently explosive mixture; it is denser than air, through which it falls and diffuses itself to a great distance; and great caution is therefor required in handling ether in a locality in which there is a light and fire, especially if the fire be near the floor.

Pure ether is neutral in reaction, but, on exposure to air or oxygen, especially in the light, it becomes acid from the formation of a small quantity of acetic acid.

Sulphuric acid mixes with ether with elevation of temperature and formation of sulphovinic acid; sulphuric anhydride forms ethyl sulphate. Nitric acid, aided by heat, oxidizes ether to carbon dioxide and acetic and oxalic acids. Ether, saturated with hydrochloric acid and distilled, yields ethyl chloride.

Chlorine, in the presence of water, oxidizes ether, with formation of aldehyde, acetic acid, and chloral. In the absence of water, however, a series of products of substitution are produced, in which two, four, and ten atoms of hydrogen are replaced by a corresponding number of atoms of chlorine. These substances in turn, by substitution of alcoholic radicals, or of atoms of elements, for atoms of chlorine, give rise to other derivatives.

Ether is largely used in the chemical arts, in pharmacy, and in the laboratory as a solvent, in the preparation of compound ethers, and for the production of cold. Its chief use in medicine is as an anæsthetic, being the safest and most readily handled that we possess. When taken in overdose it causes death, although it is by no means as liable to give rise to fatal accidents as is chloroform, and, as it seems to be without direct action upon the nerve-centres. Patients suffering from an overdose may, in the vast majority of cases, be resuscitated by artificial respiration and the induced current, one pole to be applied to the nape of the neck, and the other carried across the body just below the anterior attachments of the diaphragm.

In cases of death from ether the odor is generally well marked in the clothing and surroundings, and especially on opening the thoracic cavity. In the analysis it is sought for in the blood and lungs at the same time as chloroform (*q. v.*).

The oxides of the remaining alcoholic radicals may be obtained by processes similar to those used in the preparation of ethylic ether.

Mixed ethers differ from the simple ethers (which may be regarded as water in which both atoms of hydrogen are replaced by like alcoholic radicals, $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$—ethylic ether) in that the two atoms of hydrogen are replaced by *unlike* alcoholic radicals, $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$, methyl-ethyl oxide.

They may be readily obtained by the action of the iodide of one alcoholic radical upon the potassium or sodium oxide of the other:

$$\left.\begin{matrix}CH_3\\I\end{matrix}\right\} + \left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}O = \left.\begin{matrix}Na\\I\end{matrix}\right\} + \left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\}O$$

Methyl iodide. Ethyl sodium oxide. Sodium iodide. Ethyl methyl oxide.

As with each alcoholic iodide there can be formed as many mixed ethers as there are other monoatomic alcohols, it may be readily understood that substances of this class are very numerous.

None of them have hitherto been applied to industrial or medicinal uses.

MONOBASIC ACIDS.

Series $C_nH_{2n}O_2$.

The members of this series, although formed in a variety of ways, may be considered as derived from the alcohols of the series $C_nH_{2n+2}O$, by the substitution of an atom of oxygen for two atoms of hydrogen, by oxidation of the radical.

As the higher terms exist in the fats, and as the lower members of the series are volatile, they are frequently designated as the *volatile fatty acids.* They form an homologous series, the known terms of which are given in the table on following page.

They all exist in nature, either free or in combination as salts or ethers, some of which are important articles of food, and others substances valuable as medicinal agents.

Name.	Formula.	Fusing-point.	Boiling-point.
Formic acid	CHO_2H	1°	100°
Acetic acid	$C_2H_3O_2H$	17°	119
Propionic acid	$C_3H_5O_2H$	....	140
Butyric acid	$C_4H_7O_2H$	—20°	160
Valerianic acid	$C_5H_9O_2H$	....	175
Caproic acid	$C_6H_{11}O_2H$	9°	198
Œnanthylic acid	$C_7H_{13}O_2H$	....	212
Caprylic acid	$C_8H_{15}O_2H$	14°	236
Pelargonic acid	$C_9H_{17}O_2H$	18°	260
Capric acid	$C_{10}H_{19}O_2H$	27°	....
Lauric acid	$C_{12}H_{23}O_2H$	43.5°	....
Myristic acid	$C_{14}H_{27}O_2H$	53.8°	....
Palmitic acid	$C_{16}H_{31}O_2H$	62°	....
Margaric acid	$C_{17}H_{33}O_2H$	60°	....
Stearic acid	$C_{18}H_{35}O_2H$	69°	....
Arachic acid	$C_{20}H_{39}O_2H$	75°	....
Benic acid	$C_{22}H_{43}O_2H$	76°	....
Hyænic acid	$C_{25}H_{49}O_2H$	77°	....
Cerotic acid	$C_{27}H_{53}O_2H$	78°	....
Melissic acid	$C_{30}H_{59}O_2H$	88°	....

Formic Acid—CH_2O_2—$\left.\begin{matrix}CHO\\H\end{matrix}\right\}O$

Is widely distributed in the animal and vegetable kingdoms. As its name implies, it exists in the acid secretion of red ants, from whose bodies it was first obtained; it occurs also in the stinging hairs of certain insects, in the blood, urine, bile, perspiration, and muscular fluid of man, in the stinging-nettle, in the leaves of trees of the pine family, and, finally, in certain mineral waters.

Formic acid is also produced in a number of reactions. By the oxidation of many organic substances, sugar, starch, fibrin, gelatin, albumin, etc. By the action of potash upon chloroform and kindred bodies. By the action of mineral acids on hydrocyanic acid. During the fermentation of diabetic urine. By the direct union of carbon monoxide and water:

$$CO+H_2O=CO_2H_2.$$

By the decomposition of oxalic acid under the influence of glycerin at about 100°:

$$C_2O_4H_2 = CO_2 + CO_2H_2.$$

The last is the reaction utilized in obtaining formic acid.

It is a colorless liquid, having a sharp, acid taste, and a penetrating odor; when brought in contact with the skin it acts as a vesicant; it boils at 100° at the normal barometric pressure, and, when pure, crystallizes at 0°; it is miscible with water in all proportions.

The mineral acids decompose it into water and carbon monoxide; oxidizing agents convert it into water and carbon dioxide; alkaline hydrates decompose it with formation of a carbonate and liberation of hydrogen; it acts as a reducing agent with the salts of the noble metals.

Acetic Acid.

Acetyl hydrate—Hydrogen acetate—Pyroligneous acid—Acidum aceticum (U. S., Br.)—$C_2H_3O_2H$—$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$.—Although in its dilute form, as vinegar, it has been known from remote antiquity, the pure acid was only obtained in the last century.

It is produced in a great number of reactions, the principal of which are:

First.—By the oxidation of alcohol:

$$C_2H_6O+O_2=C_2H_4O_2+H_2O.$$

Second.—By the dry distillation of wood.

Third.—By the decomposition of natural acetates by mineral acids.

Fourth.—By the action of potash in fusion on sugar, starch, oxalic, tartaric, citric acids, etc.

Fifth.—By the decomposition of gelatin, fibrin, casein, etc., by sulphuric acid and manganese dioxide.

Sixth.—By the action of carbon dioxide upon sodium methyl:

$$CO_2+NaCH_3=C_2H_3O_2Na,$$

and decomposition of the sodium acetate so produced.

The acetic acid used in the arts and in pharmacy is prepared by the destructive distillation of wood, which is heated in an iron retort connected with a condensing system. The products of the distillation, which vary with the nature of the wood used, are numerous. Charcoal remains in the retort, while the distilled product consists of an acid, watery liquid, a tarry material, and gaseous products. One hundred parts of wood yield usually:

Charcoal	28—30 parts.
Acid water	23—30 parts.
Tar	7—10 parts.
Gas	37—30 parts.

The gases are carbon dioxide, carbon monoxide, and hydrocarbons; they are sometimes used for illuminating purposes, but are usually directed into the furnace, where they serve as fuel. The tar is a mixture of empyreumatic oils, hydrocarbons, phenol, oxyphenol, acetic acid, ammonium acetate, etc., and is used almost exclusively for the preservation of cordage and wood in ships.

The acid water is very complex, and contains, besides acetic acid, formic, propionic, butyric, valerianic, and oxyphenic acids, acetone, naphthalene, benzene, toluene, cumene, creasote, methyl alcohol, and methyl acetate, etc. Partially freed from tar by decantation, it is a brown, acid liquid, having a disagreeable, empyreumatic odor. It still contains about twenty per cent. of tarry and oily material, and about four per cent. of acetic acid; this is the *crude pyroligneous acid* of commerce.

The crude product is subjected to a first purification by distillation; the first portions are collected separately and yield methyl alcohol (*q. v.*); the remainder of the distillate is the *distilled pyroligneous acid* of com-

merce, used to a limited extent as an antiseptic, but principally for the manufacture of acetic acid and the acetates. It can only be freed from the impurities which it still contains by chemical means; to this end slacked lime and chalk are added, at a gentle heat, to neutralization; the liquid is boiled and allowed to settle twenty-four hours; the clear liquid, which is a solution of calcium acetate, is decanted and evaporated; the calcium salt is converted into sodium acetate, which is then purified by calcination at a temperature below 330°, dissolved, filtered, and recrystallized; the salt is then decomposed by a proper quantity of sulphuric acid, and the liberated acetic acid separated by distillation.

The product so obtained is a solution of acetic acid in water, containing thirty-six per cent. of true acetic acid, and being of sp. gr. 1.047, United States (the acid of the British Pharmacopœia is weaker—thirty-three per cent., $C_2H_4O_2$, and sp. gr. 1.044).

When pure acetic acid is required, recourse is had to the decomposition of a dry acetate by heat; it is known as *glacial* acetic acid.

Acetic acid is a colorless liquid at ordinary temperatures; below 17°, when pure, it is a crystalline solid. It boils at 119°; sp. gr. 1.0801 at 0°; its odor is penetrating and acid; when brought in contact with the skin it destroys the epidermis and causes vesication; it mixes with water in all proportions, the mixtures being less in volume than the sum of the volumes of the constituents. The specific gravities of the mixtures gradually increase up to that containing twenty-three per cent. of water, after which they again diminish, and all the mixtures containing more than forty-three per cent. of acid are of higher specific gravity than the acid itself. In the following table are given the specific gravity of acids of different degrees of concentration at 15° C.:

Acetic acid, per cent.	Specific gravity.	Acetic acid, per cent.	Specific gravity.	Acetic acid, per cent.	Specific gravity.	Acetic acid, per cent.	Specific gravity.
0	0.9992	26	1.0363	51	1.0623	76	1.0747
1	1.0007	27	1.0375	52	1.0631	77	1.0748
2	1.0022	28	1.0388	53	1.0638	78	1.0748
3	1.0037	29	1.0400	54	1.0646	79	1.0748
4	1.0052	30	1.0412	55	1.0653	80	1.0748
5	1.0067	31	1.0424	56	1.0660	81	1.0747
6	1.0083	32	1.0436	57	1.0666	82	1.0746
7	1.0098	33	1.0447	58	1.0673	83	1.0744
8	1.0113	34	1.0459	59	1.0679	84	1.0742
9	1.0127	35	1.0470	60	1.0685	85	1.0739
10	1.0142	36	1.0481	61	1.0691	86	1.0736
11	1.0157	37	1.0492	62	1.0697	87	1.0731
12	1.0171	38	1.0502	63	1.0702	88	1.0726
13	1.0185	39	1.0513	64	1.0707	89	1.0720
14	1.0200	40	1.0523	65	1.0712	90	1.0713
15	1.0214	41	1.0533	66	1.0717	91	1.0705
16	1.0228	42	1.0543	67	1.0721	92	1.0696
17	1.0242	43	1.0552	68	1.0725	93	1.0686
18	1.0256	44	1.0562	69	1.0729	94	1.0674
19	1.0270	45	1.0571	70	1.0733	95	1.0660
20	1.0284	46	1.0580	71	1.0737	96	1.0644
21	1.0298	47	1.0589	72	1.0740	97	1.0625
22	1.0311	48	1.0598	73	1.0742	98	1.0604
23	1.0324	49	1.0607	74	1.0744	99	1.0580
24	1.0337	50	1.0615	75	1.0746	100	1.0553
25	1.0350						

The vapor of acetic acid burns with a pale, bluish flame; when passed through a tube heated to redness it is decomposed, a mixture of combustible gases being given off and a carbonaceous residue remaining in the tube. The pure acid only decomposes calcic carbonate when diluted with water; and when mixed with alcohol does not redden litmus paper.

Sulphuric acid, aided by heat, decomposes and blackens acetic acid; sulphur and carbon dioxides are given off. The presence of acetic acid may be recognized by this and by the following reactions: with silver nitrate, a white, crystalline precipitate, partially dissolved by heat; no reduction of silver on boiling the mixture. When it is heated with small quantities of alcohol and sulphuric acid, acetic ether is given off, and may be recognized by its odor. When an acetate is calcined with a small quantity of arsenic trioxide, the foul odor of cacodyl oxide is observed.

Chlorine acts upon acetic acid slowly under ordinary conditions, but actively under the influence of direct sunlight, producing *monochloracetic acid*, $C_2H_3ClO_2$; *dichloracetic acid*, $C_2H_2Cl_2O_2$; and *trichloracetic acid*, $C_2HCl_3O_2$. The last-named is obtained by exposing glass-stoppered bottles (well closed) filled with dry chlorine, and containing a small quantity of glacial acetic acid, to the direct rays of the sun for a day or more. It it an odorless, crystalline solid, which fuses at 46°, and distils at 195°—200°. It is strongly acid, and has been used in medical practice as a powerful vesicant.

Acetic acid is used in pharmacy in the preparation of many substances. The *Acidum aceticum dilutum* (U. S., Br.) is of sp. gr. 1.006, and contains 4.5 per cent. of true acetic acid; its chief use is in the preparation of the *aceta* or *medicated vinegars*, improperly so called, which, whether they be made with dilute acetic acid, or with distilled vinegar, do not contain those constituents of vinegar which distinguish it from dilute acetic acid.

Vinegar is an acid liquid owing its acidity to acetic acid, and holding certain fixed and volatile substances in solution. It has been known from early antiquity, and was the only acid known up to the end of the eighth century, when the Arabian alchemist Djafar, or Geber, as he is frequently called, discovered nitric acid.

It is obtained from some liquid containing ten per cent. or less of alcohol, which is converted into acetic acid, either by simple oxidation, as under the influence of platinum black, or, as in the industrial manufacture of vinegar, by the transferring of atmospheric oxygen to the alcohol during the process of nutrition of a peculiar vegetable ferment, known as *mycoderma aceti* or, popularly, as *mother of vinegar*. Vinegar is now manufactured principally by one or two processes—the German method and that of Pasteur. In the former, the alcoholic fluid, which must also contain albuminous matter, is allowed to trickle slowly through barrels in which it meets near the top a diaphragm, pierced with a number of holes, through which pass short cords; from these it drops upon a thick layer of beech-wood shavings, supported by a perforated false bottom. By a suitable arrangement of holes and tubes, an ascending current of air is made to pass through the barrel. The acetic ferment clings to the cords and shavings, and under its influence acetification takes place rapidly, owing to the large surface exposed to the air.

In Pasteur's process, which has to a great extent superseded the process formerly followed at Orleans, the ferment is sown upon the surface of the alcoholic liquid, contained in large, shallow, covered vats, from which the vinegar is drawn off after acetification has been com-

pleted; the mother is collected, washed, and used in a subsequent operation.

The liquids from which vinegar is made are wine, cider, and beer, to which dilute alcohol is frequently added; the most esteemed being that obtained from white wine.

Wine vinegar has a pleasant, acid taste and odor; it consists of water, acetic acid (about five per cent.), potassium bitartrate (about 2.5 grams per litre), alcohol, acetic ether, glucose, malic acid, mineral salts present in wine, a fermentescible, nitrogenized substance, coloring matter, etc. Its specific gravity is 1.020 to 1.025; its color varies from a pale yellow to a light reddish brown, according as it is made from white or red wine. When evaporated, it yields from 1.7 to 2.4 per cent. of solid residue.

Vinegars made from alcoholic liquids other than wine contain no potassium bitartrate, contain less acetic acid, and have not the aromatic odor of wine vinegar. Cider vinegar is of sp. gr. 2.0; is yellowish, has an odor of apples, and yields 1.5 per cent. of extract on evaporation. Beer vinegar is of sp. gr. 3.2; has a bitterish flavor, and an odor of sour beer; it leaves six per cent. of extract on evaporation.

The principal *adulterations* of vinegar are: *sulphuric acid*, whose presence is indicated by an increase in the specific gravity, or more certainly, by adding a few drops of the vinegar to some fragments of cane-sugar, and evaporating over the water-bath to dryness; in the presence of sulphuric acid the residue is dark brown or black. As commercial sulphuric acid always contains arsenic, that element has frequently been detected in adulterated vinegars. *Water*, an excess of which is indicated by a low power of saturation of the vinegar, in the absence of mineral acids. Two parts of good wine vinegar neutralize ten parts of sodium carbonate; the same quantity of cider vinegar, 3.5 parts; and of beer vinegar, 2.5 parts of carbonate. *Pyroligneous acid* may be detected by the creosote-like odor and taste. *Pepper*, *capsicum*, and other acrid substances, are often added to communicate fictitious strength; in vinegar so adulterated an acrid odor is perceptible after neutralization of the acid with sodium carbonate. *Copper*, *zinc*, *lead*, *and tin* frequently occur in vinegar which has been in contact with those elements, either during the process of manufacture or subsequently; they may be detected by methods elsewhere described.

Distilled vinegar, *Acetum destillatum* (U. S.), is prepared by distilling vinegar in glass vessels; it contains none of the fixed ingredients of vinegar, but its volatile constituents (acetic acid, water, alcohol, acetic ether, odorous principles, etc.), and a small quantity of aldehyde. It is a limpid, wholly volatile liquid, whose odor is similar to, but weaker than that of the kind of vinegar from which it was distilled, from which it also differs in being of less acid strength, as the boiling-point of acetic acid is higher than that of water. Dilute acetic acid is frequently called distilled vinegar.

When dry acetate of copper is distilled, a blue, strongly acid liquid passes over; this, upon rectification, yields a colorless, mobile liquid, which boils at 56° C., has a peculiar odor, and is a mixture of acetic acid, water, and acetone, known to the older chemists as *radical vinegar*, and still used under that name in perfumery.

Toxicology.—When taken internally, acetic acid and vinegar (the latter in doses of four to five fl. ʒ) act as irritants and corrosives, causing in some instances perforation of the stomach, and death in from six to fifteen hours. Milk of magnesia should be given as an antidote, with the view to neutralizing the acid.

The presence of acetic acid, or of an acetate, may be recognized by the following *tests:*

First.—When heated with sulphuric acid, acetic acid, recognizable by its odor, is given off.

Second.—If a mixture of an acetate, sulphuric acid, and alcohol be heated, the apple odor of ethyl acetate is produced.

Third.—Neutral solution of ferric chloride forms, with a neutral solution of an acetate, a deep red liquid, which turns yellow on the addition of a free acid.

Propionic Acid, $C_3H_6O_2$—$\left.\begin{matrix}C_3H_5O\\H\end{matrix}\right\}O$.

This acid, discovered by Gottlieb in 1844, is formed in many decompositions of organic substances. By the action of caustic potassa upon sugar, starch, gum, and ethyl cyanide; during fermentation, vinous or acetic, in wine, moist leather, calcium tartrate solution; in the distillation of wood, and during the putrefaction of peas, beans, etc.; by the oxidation of normal propylic alcohol, etc. It is best prepared by heating ethyl cyanide with potash until the odor of the ether has disappeared; the acid is then liberated from its potassium compound by sulphuric or phosphoric acid, and purified.

It is a colorless liquid, sp. gr. 0.996, does not solidify at —21°, boils at 140°, mixes with water and alcohol in all proportions, resembles acetic acid in odor and taste. Its salts are soluble and crystallizable.

Propionic acid is probably formed in the body as a product of oxidation of the fats and albuminoids, its presence, however, has not been demonstrated with certainty, although it has been said to exist in the perspiration, the contents of the stomach, in the vomit of cholera, and in fermented diabetic urine.

Butyric Acid, $\left.\begin{matrix}C_4H_7O\\H\end{matrix}\right\}O$——$CH_2$—$CH_2$—$CH_2$—$CO,OH$.

Discovered by Chevreul in butter; it exists in nature free and in combination, in its ethylic and glyceric ethers. It has been found in the milk, perspiration, muscular fluid, the juices of the spleen and of other glands, the urine, contents of the stomach and large intestine, fæces, and guano, in certain fruits, in yeast, in the products of decomposition of many vegetable substances, and in natural waters; in fresh butter in small quantity, more abundantly in that which is rancid.

It is formed in a number of decompositions of organic substances. By the action of sulphuric acid and manganese dioxide, aided by heat, upon cheese, starch, gelatin, etc.; during the combustion of tobacco (as ammonium butyrate); by the action of nitric acid upon oleic acid; during the putrefaction of fibrin and other albuminoids; during a peculiar fermentation of glucose and starchy material in the presence of casein or gluten. This fermentation, known as the butyric, takes place in two stages; at first the glucose is converted into lactic acid:

$$C_6H_{12}O_6=2\,(C_3H_6O_3),$$

and this in turn is decomposed into butyric acid, carbon dioxide, and hydrogen:

$$2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2.$$

Butyric acid is now usually obtained from the animal charcoal which has been used in the purification of glycerine, in which it exists as calcium butyrate. It is also formed by subjecting to fermentation, at 25°—30°, a mixture composed of glucose 1 kilo, water to sp. gr. 10° Baumé, chalk 0.5 kilo, cheese or gluten 0.1 kilo. The calcium butyrate is decomposed by sulphuric acid, and the butyric acid separated by distillation.

Butyric acid is a colorless, mobile liquid, having a disagreeable, persistent odor of rancid butter, and a sharp, acid taste, soluble in water, alcohol, ether, and methyl alcohol; boils at 164°, distilling unchanged; solidifies in a mixture of solid carbon dioxide and ether; sp. gr. 0.974 at 15°; a good solvent of fats.

Sulphuric acid does not act upon butyric acid in the cold, and only slightly under the influence of heat. Nitric acid dissolves it unaltered in the cold, but, on the application of heat, oxidizes it to succinic acid. Dry chlorine under the influence of sunlight, and bromine under the influence of heat and pressure, form products of substitution with butyric acid. It readily forms ethers and salts, the latter being, for the most part, soluble in water. Its vapor is inflammable and burns with a blue flame.

Butyric acid is formed in the intestine, by the process of fermentation mentioned above, at the expense of those portions of the carbohydrate elements of food which escape absorption, and is discharged with the fæces as ammonium butyrate.

Isobutyric acid, an isomere of butyric acid, which boils at 152°, has also been found in human fæces. It corresponds to isobutyl alcohol, and has the composition—

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH—CO,OH.$$

Valerianic Acids, $C_5H_{10}O_2 — \left.\begin{matrix} C_5H_9O \\ H \end{matrix}\right\} O.$

Corresponding to the four primary amylic alcohols, there are four amylic or valerianic acids:

I. $CH_3—CH_2—CH_2—CH_2—CO,OH.$

II. $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH—CH_2—CO,OH.$

III. $CH_3—CH_2—\overset{CH_3}{\underset{}{\overset{}{\underset{}{>}}}}CH—CO,OH.$

IV. $\begin{matrix} CH_3 \\ CH_3—C—CO,OH. \\ CH_3 \end{matrix}$

I. **Normal valerianic acid**—*Butylformic acid—Propylacetic acid*—is obtained by the oxidation of normal amylic alcohol. It is an oily liquid, boils at 184°—185°, and has an odor resembling that of butyric acid.

II., III. **Ordinary valerianic acid**—*Delphinic acid—Phocenic acid—Isovaleric acid—Isopropyl acetic acid—Isobutylformic acid—Acidum valerianicum* (U. S., Br.).—This acid was discovered in 1817 by Chevreul, in the oil of the porpoise (*delphinium phocœna*), and subsequently in valerian root and in angelica root. It is formed during putrid fermentation or oxidation of albuminoid substances. It occurs in the urine and fæces in typhus, variola, and acute atrophy of the liver. It is also formed in a variety of chemical reactions and notably by the oxidation of amylic alcohol.

It is prepared either by distilling water from valerian root, or, more economically, by mixing rectified amylic alcohol with sulphuric acid, adding, when cold, a solution of potassium dichromate, and distilling after the reaction has become moderated; the distillate is neutralized with sodium carbonate; and the acid is obtained from the sodium valerianate so produced, by decomposition by sulphuric acid and rectification.

The properties and nature of the acid differ according to those of the amyl alcohol from which it is obtained. The active alcohol yields the acid,

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH—CH_2—CO,OH,$$

which is itself optically active, which forms an uncrystallizable and exceedingly soluble barium salt, and whose boiling-point is 172.5°—173.5°. The inactive alcohol yields by oxidation the acid, $\begin{matrix}CH_3\\CH_2—CH_2\end{matrix}\!\!>\!CH—CO,OH$, which is optically inactive, whose barium salt is readily crystallizable and soluble in water to the extent of forty-eight parts in one hundred, and whose boiling-point is 174.5°.

The identity of the acid obtained from valerian root and that obtained by the oxidation of amylic alcohol has frequently been called in question. The properties of the former show, however, that it is identical with the acid obtained by the oxidation of *optically inactive* amylic alcohol. The artificial product, being obtained from the commercial mixture of active and inactive alcohols, is a mixture in different proportions of the two acids mentioned above.

The ordinary valerianic acid is an oily, colorless liquid, having a penetrating odor, and a sharp, acrid taste. It solidifies at —16°; boils at 173°—175°; sp. gr. 0.9343—0.9465 at 20°; burns with a white, smoky flame. It dissolves in thirty parts of water, and in alcohol and ether in all proportions. It dissolves phosphorus, camphor, and certain resins. It forms salts and ethers called *valerianates*, some of which, as those of ammonium, zinc, quinine, atropine, bismuth, and iron, are used in medicine.

IV. *Trimethyl acetic acid—Pivalic acid*—is a crystalline solid, which fuses at 35.5° and boils at 163.7°; sparingly soluble in water; obtained by the action of cyanide of mercury upon tertiary butyl iodide.

Caproic Acids.

Hexylic acids—$C_6H_{12}O_2$—$\left.\begin{matrix}C_6H_{11}O\\H\end{matrix}\right\}O$.—There probably exist quite a number of isomeres having the composition indicated above, some of which have been prepared from butter, cocoa-oil, and cheese, and by decomposition of amyl cyanide, or of hexyl alcohol.

The acid obtained from butter, in which it exists as a glyceric ether, is a colorless, oily liquid, boils at 205°; sp. gr. 0.931 at 15°; has an odor of perspiration and a sharp, acid taste; is very sparingly soluble in water, but soluble in alcohol. The acid obtained from amyl cyanide deviates the plane of polarization to the right ($[a]r = 2.43°$); boils at 198°, and solidifies at −9°.

Œnanthylic Acid.

Heptylic acid, $C_7H_{14}O_2$—$\left.\begin{matrix}C_7H_{13}O\\H\end{matrix}\right\}$O—exists in spirits distilled from rice and maize, and is formed by the action of nitric acid upon fatty substances, especially upon castor oil. It is a colorless oil; boils at 212°; sp. gr. 0.9167 at 24°; soluble in alcohol and in ether.

Caprylic Acid.

Octylic acid, $C_8H_{16}O_2$—$\left.\begin{matrix}C_8H_{15}O\\H\end{matrix}\right\}$O—accompanies caproic acid in butter, cocoa-oil, etc. It is solid, melts at 14°—15°, and boils at 236°; almost insoluble in water; very soluble in alcohol and in ether.

Pelargonic Acid.

Nonylic acid, $C_9H_{18}O_2$—$\left.\begin{matrix}C_9H_{17}O\\H\end{matrix}\right\}$O—exists in the volatile oil of geranium, and is formed by the action of nitric acid upon essence of rue. It is a colorless oil; has a feeble odor; solidifies at 10°; boils at 260°; insoluble in water; soluble in alcohol and ether.

Capric Acid.

Decylic acid, $C_{10}H_{20}O_2$—$\left.\begin{matrix}C_{10}H_{19}O\\H\end{matrix}\right\}$O—exists in butter, cocoa-oil, etc., associated with caproic and caprylic acids in their glyceric ethers, and in the residues of distillation of Scotch whiskey, as amyl caprate. It is a white, crystalline solid; melts at 27.5°; boils at 273°; insoluble in water; soluble in alcohol and ether; has a faint odor, resembling that of the goat.

Lauric Acid.

Laurostearic acid, $C_{12}H_{24}O_2$—$\left.\begin{matrix}C_{12}H_{23}O\\H\end{matrix}\right\}$O—exists in laurel berries, cocoa-butter, and in other vegetable fats. It is a transparent, crystalline solid; melts at 43.5°; insoluble in water; readily soluble in alcohol and in ether.

Myristic Acid, $C_{14}H_{28}O_2$—$\left.\begin{matrix}C_{14}H_{27}O\\H\end{matrix}\right\}$O,

Exists in many vegetable oils, in cow's butter, and in spermaceti. It crystallizes in brilliant, colorless plates; fusible at 54°.

Palmitic Acid.

Ethalic acid, $C_{16}H_{32}O_2$—$\left.\begin{matrix}C_{16}H_{31}O\\H\end{matrix}\right\}$O—exists in palm-oil, in combination when the oil is fresh, and free when the oil is old; it also enters into the composition of nearly all animal and vegetable fats. It is obtained from the fats, palm-oil, etc., by saponification with caustic potassa (see p. 285), and subsequent decomposition of the soap by a strong acid. It is also formed by the action of caustic potash in fusion upon cetyl alcohol (ethal), and by the action of the same reagent upon oleic acid.

Palmitic acid is a white, crystalline solid; odorless; tasteless; lighter than water, in which it is insoluble; quite soluble in alcohol and in ether; fuses at 62°; distils unchanged with vapor of water. It is used in the manufacture of candles and of soaps.

Margaric Acid, $C_{17}H_{34}O_2$—$\left.\begin{matrix}C_{17}H_{33}O\\H\end{matrix}\right\}$O.

Previous to 1852 this acid was supposed to exist as a glyceride in all fats, solid and liquid; in that year, however, Heintz showed that what had been taken for margaric acid was a mixture of ninety per cent. of palmitic and ten per cent. of stearic acid, and at the same time he obtained the true margaric acid by the action of potassium hydrate upon cetyl cyanide.

It is a white, crystalline body; fusible at 59.9°; insoluble in water; soluble in alcohol and in ether.

Stearic acid, $C_{18}H_{36}O$—$\left.\begin{matrix}C_{18}H_{35}O\\H\end{matrix}\right\}$O.

This, the most abundant of the fatty acids, was discovered by Chevreul in 1811. It exists as a glyceride in all solid fats, and in many oils, and also free to a limited extent.

To obtain it pure, the fat is saponified with an alkali, and the soap decomposed by hydrochloric acid; the mixture of fatty acids is dissolved in a large quantity of alcohol, and the boiling solution *partly* precipitated by the addition of a concentrated solution of barium acetate. The precipitate is collected, washed, and decomposed by hydrochloric acid; the stearic acid which separates is washed and recrystallized from alcohol. The process is repeated until the product fuses at 70°.

An impure stearic acid, mixed with palmitic and other acids, is prepared industrially on a large scale in the manufacture of stearin candles.

Pure stearic acid is a colorless, odorless, tasteless solid; fusible at 69°—70°; unctuous to the touch; insoluble in water; very soluble in alcohol and in ether. The alkaline stearates are soluble in water; those of calcium, barium, and lead are insoluble.

Stearic and palmitic acids exist free in the intestine during the digestion of fats, a portion of which is decomposed by the action of the pancreatic secretion into fatty acids and glycerin. The same decomposition also occurs in the presence of putrefying albuminoid substances.

Arachic acid, $C_{20}H_{40}O_2$—$\left.\begin{matrix}C_{20}H_{39}O\\H\end{matrix}\right\}$O—exists as a glyceride in peanut-oil (now largely used as a substitute for olive-oil), in oil of ben, and

in small quantity in butter. It is a crystalline solid, which melts at 75°, and solidifies at 73°; sparingly soluble in aqueous alcohol; soluble in absolute alcohol and ether.

Benic acid—*Benostearic acid*—$C_{22}H_{44}O_2$—$\left.\begin{matrix}C_{22}H_{43}O\\H\end{matrix}\right\}O$—a solid, crystalline body; fuses at 76°; solidifies at 70°; exists in oil of ben.

Hyænic acid, $C_{32}H_{64}O_2$—$\left.\begin{matrix}C_{32}H_{63}O\\H\end{matrix}\right\}O$—exists in the fat, and especially in the anal glands, of the hyena.

Cerotic acid, $C_{27}H_{54}O_2$—$\left.\begin{matrix}C_{27}H_{53}O\\H\end{matrix}\right\}O$—constitutes the bulk of that part of beeswax which is soluble in boiling alcohol, and may be obtained from China wax by dry distillation.

Melissic acid, $C_{30}H_{60}O_2$—$\left.\begin{matrix}C_{30}H_{59}O\\H\end{matrix}\right\}O$—exists in beeswax.

COMPOUND ETHERS.

Methylic.

Methyl nitrate, $\left.\begin{matrix}NO_2\\CH_3\end{matrix}\right\}O$—is prepared by bringing together, in a retort, powdered potassium nitrate and a mixture of sulphuric acid and methyl alcohol; the action takes place at first in the cold, but the distillation must be completed at the temperature of the water-bath. The distillate is purified by washing with water, and by repeated rectifications from massicot and calcium chloride.

It is a colorless liquid; sp. gr. 1.182 at 22°; boils at 66°; burns with a yellow flame; its vapor detonates violently when heated above 150°. It is decomposed by potash into potassium nitrate and methylic alcohol; it dissolves ammonia, with formation of ammonium nitrate and methylamine. It is a good solvent of nitro-glycerine and of gun-cotton.

Methyl nitrite, $\left.\begin{matrix}NO\\CH_3\end{matrix}\right\}O$—is obtained by heating methylic alcohol with nitric acid and copper. Below −12° it is a yellowish liquid; above that temperature, a gas. Isomeric with nitromethane.

Ethylic.

Ethyl nitrate—*Nitric ether*—$\left.\begin{matrix}NO_2\\C_2H_5\end{matrix}\right\}O$—is obtained by distilling a mixture of one volume of nitric acid and two volumes of alcohol, in the presence of urea, the last-named substance being added to prevent the formation of the lower oxides of nitrogen. The first part of the distillate, consisting of alcohol, is discarded, and the distillation is stopped when the contents of the retort have been reduced to one-third the original bulk. The product is washed, dried by contact with calcium chloride, and rectified.

Nitric ether is a colorless liquid, has a sweet taste, with a bitter after-taste; sp. gr. 1.112 at 17°; boils at 85°—86°; burns with a white flame. Its vapor, when heated, explodes violently on the approach of a flame.

Ethyl nitrite—*Nitrous ether*—$\left.\begin{matrix}NO\\C_2H_5\end{matrix}\right\}O$—was obtained by Kunkel as early as 1681.

Quite a number of processes have been suggested for obtaining this substance; the best consists of directing the nitrous fumes, produced by the action of nitric acid upon starch, under the influence of heat, into alcohol contained in a retort connected with a well-cooled receiver.

An older process, still frequently used, is by acting upon alcohol directly with nitric acid; the operation must be conducted in a capacious retort, and the gentle heat applied to start the reaction must be withdrawn as soon as the distillation begins. This method cannot be used on a large scale, owing to the violence of the action, and is also objectionable on account of the loss of alcohol required to reduce the nitric acid.

Pure ethylic nitrate is a yellowish liquid; has a peculiar, apple-like odor, and a sweetish, sharp taste; sp. gr. 0.947; boils at 18°. Its vaporization produces a great diminution of temperature; the vapor is inflammable, burning with a white flame; very sparingly soluble in water; quite soluble in alcohol and ether.

It is decomposed by warm water into alcohol, nitric acid, and nitrogen dioxide; more rapidly by alkalies, with formation of malate and nitrate of the alkaline element, but without formation of acetate. It is energetically attacked by sulphuric acid, and also by sulphydric acid and the alkaline sulphides. Its vapor, when passed through a red-hot tube, is decomposed, yielding nitrogen, nitrogen dioxide, carbon monoxide, hydrocarbons, water, ammonium cyanide and carbonate, an oily material, and carbon. When kept it is liable to spontaneous decomposition into nitrogen dioxide and malic acid, especially in the presence of water.

Its vapor rapidly produces anæsthesia; it is not, however, used in medicine in its pure form, but only in alcoholic solution: *Spiritus ætheris nitrosi* (U. S., Br.), which also contains aldehyde. Owing to the presence of the last-named substance, and to the presence of water, the spirit is very liable to become acid, either from the formation of acetic acid by the oxidation of the aldehyde, or from the decomposition of the ether under the influence of water; a change which renders it unfit for use in many of the prescriptions in which it is frequently used, especially in that with potassium iodide, from which it liberates iodine. The presence of free acid may be detected by effervescence when the spirit is shaken with hydrosodic carbonate. Its acidity may be corrected by shaking with potassium carbonate, and decanting, provided it does not contain water.

Ethyl borates.—There are four ethylic borates, three of which correspond to the three acids, boric, metaboric, and tetraboric. The borate, $BO_3(C_2H_5)_3$, is a colorless, mobile liquid, having a peculiar, agreeable odor, and a bitter taste; soluble, but decomposed, by water; soluble in alcohol and ether; burns with a green flame, giving off dense fumes of boric acid.

Ethyl phosphates.—Four of these compounds are known:

$PO_4(C_2H_5)H_2$—Monethyl-phosphoric acid—Phosphovinic acid.
$PO_4(C_2H_5)_2H$—Diethyl-phosphoric acid.
$PO_4(C_2H_5)_3$—Triethyl phosphate—Phosphoric ether.
$P_2O_7(C_2H_5)_4$—Tetrethylic pyrophosphate—Pyrophosphoric ether.

Of these, the first two possess acid properties and form salts. There exist also numerous compounds similar in constitution to the ethyl phosphates, in which one or more of the atoms of oxygen are replaced by

atoms of sulphur, or of selenium, *e. g.*, diethyl-sulphophosphoric acid, $PO_2S(C_2H_5)_2H$, some of which also form salts.

There are also four ethyl phosphites, two of which are acids and two neutral ethers.

Ethyl sulphates.—These are two in number:

$SO_4(C_2H_5)$—HEthyl-sulphuric, or sulphovinic acid.
$SO_4(C_2H_5)_2$—Ethyl-sulphate—Sulphuric ether.

Ethyl-sulphuric acid, $\left.\begin{matrix}SO_2\\(C_2H_5)\\H\end{matrix}\right\}O_2$—is formed as an intermediate product in the manufacture of ethylic ether (*q. v.*). It is prepared by slowly adding sulphuric acid to an equal volume of alcohol, mixing and cooling as the addition progresses; when cold, the mixture is diluted with water, and barium carbonate is added to saturation; the clear liquid, on concentration, yields crystalline plates of barium ethyl-sulphate $[SO_4(C_2H_5)]_2Ba''$, which, when exactly decomposed with sulphuric acid, liberates sulphovinic acid.

Pure ethyl-sulphuric acid is a colorless, syrupy, highly acid liquid; sp. gr. 1.316; soluble in water and alcohol in all proportions; insoluble in ether.

It decomposes slowly at ordinary temperatures, more rapidly when heated. When heated alone or with alcohol, it yields ether and sulphuric acid:

$$\left.\begin{matrix}SO_2\\(C_2H_5)\\H\end{matrix}\right\}O_2 + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2.$$

When heated with water, it yields alcohol and sulphuric acid:

$$\left.\begin{matrix}SO_2\\(C_2H_5)\\H\end{matrix}\right\}O_2 + \left.\begin{matrix}H\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2.$$

It forms crystalline salts, known as *sulphovinates*, one of which, *sodium sulphovinate*, $SO_4(C_2H_5)Na$, has been used in medicine. It is a white, deliquescent solid, either crystalline with 10.78 per cent. of water of crystallization, or granular and anhydrous; the former fuses at 86°, the latter does not fuse, but is decomposed at 100°; it is soluble in 0.61 parts of water at 17°. Its solution should give no precipitate with barium chloride.

Ethyl sulphate, $\left.\begin{matrix}SO_2\\(C_2H_5)_2\end{matrix}\right\}O_2$—the true sulphuric ether, is obtained by passing vapor of sulphur trioxide into *pure* ethylic ether, thoroughly cooled; the product is purified by washing with water and milk of lime, and concentrating in vacuo.

It is a colorless, oily liquid, has a sharp, burning taste, and the odor of peppermint; sp. gr. 1.120; it cannot be distilled without decomposition; in contact with water it is decomposed with formation of sulphovinic acid.

By the action of an excess of sulphuric acid upon alcohol, by the dry distillation of the sulphovinates, and in the last stages of manufacture of ether, a yellowish, oily liquid, having a penetrating odor and a sharp, bitter taste, is formed; this is *sweet* or *heavy oil of wine*, and its ethereal

solution is *Oleum æthereum* (U. S.). It seems to be a mixture of ethyl-sulphate with hydrocarbons of the series C_nH_{2n}. On contact with water or an alkaline solution, it is decomposed, sulphovinic acid is formed, and there separates a colorless oil, of sp. gr. 0.917, boiling at 280°, which is *light oil of wine.* This oil is polymeric with ethylene, and is probably *cetene*, $C_{16}H_{32}$; it is sometimes called *etherine* or *etherol;* when cooled to −35° it deposits crystals, which fuse at 110° and boil at 260°.

Ethyl acetate—*Acetic ether*—$\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}$O—is obtained by distilling a mixture of potassium or sodium acetate, sulphuric acid, and alcohol; the distillate is purified by washing with an alkaline solution and with water, dried by contact with calcium chloride, and rectified. It may also be obtained by passing carbon dioxide through an alcoholic solution of potassium acetate, and purifying as above.

It is a colorless liquid; has an agreeable, ethereal odor; boils at 74°; sp. gr. 0.89 at 15°; soluble in six parts water, and in all proportions in methyl and ethyl alcohols and in ether; a good solvent of essences, resins, cantharidine, morphine, gun-cotton, and, in general, of substances soluble in ether; burns with a yellowish white flame.

Chlorine acts energetically upon ethyl acetate, producing products of substitution, varying according to the intensity of the light from $C_4H_6Cl_2O_2$ to $C_4Cl_6O_2$.

Ethyl formiate—*Formic ether*—$\left.\begin{matrix}CHO\\C_2H_5\end{matrix}\right\}$O—is obtained by decomposition of a formiate by a process similar to that used in the preparation of the acetate, also by distilling a mixture of glycerin, oxalic acid, and alcohol; it is also formed in the manufacture of fulminating mercury. It is obtained as a commercial product by distilling a mixture of starch, alcohol, water, sulphuric acid, and manganese dioxide.

It is a colorless liquid; has an odor resembling that of the peach; boils at 56°; sp. gr. 0.915 at 18°; burns with bluish flame; soluble in nine parts of water, and in all proportions in alcohol and ether.

It is isomeric with methyl acetate:

$\left.\begin{matrix}CHO\\C_2H_5\end{matrix}\right\}$O $C_3H_6O_2$ — Ethyl formiate.

$\left.\begin{matrix}C_2H_3O\\CH_3\end{matrix}\right\}$O $C_3H_6O_2$ — Methyl acetate.

The different arrangement of the atoms in the molecule is well shown by the action of alkalies upon the two substances, producing ethylic alcohol and a formiate in one case, and methylic alcohol and an acetate in the other.

$$\underset{\text{Ethyl formiate.}}{\left.\begin{matrix}CHO\\C_2H_5\end{matrix}\right\}O} + \underset{\text{Potassium hydrate.}}{\left.\begin{matrix}K\\H\end{matrix}\right\}O} = \underset{\text{Potassium formiate.}}{\left.\begin{matrix}CHO\\K\end{matrix}\right\}O} + \underset{\text{Ethyl hydrate.}}{\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O}$$

$$\underset{\text{Methyl acetate.}}{\left.\begin{matrix}C_2H_3O\\CH_3\end{matrix}\right\}O} + \underset{\text{Potassium hydrate.}}{\left.\begin{matrix}K\\H\end{matrix}\right\}O} = \underset{\text{Potassium acetate.}}{\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O} + \underset{\text{Methyl hydrate.}}{\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O}$$

Ethyl acetate and formiate are largely used in combination with other compound ethers of methyl, ethyl, and amyl in the manufacture of *fruit-*

essences, which, with the exception of essence of orange, are rarely, if ever, made from the fruits after which they are named. In the following table is given the composition, in cubic centimetres, added to one hundred parts of alcohol, of the principal artificial essences used in the manufacture of confectionery. The constituents used must be chemically pure:

ARTIFICIAL FRUIT-ESSENCES.

	Glycerin.	Chloroform.	Nitric ether.	Aldehyde.	Ethyl acetate.	Ethyl formiate.	Ethyl butyrate.	Ethyl valerianate.	Ethyl benzoate.	Ethyl œnanthylate.	Ethyl sebate.	Methyl salicylate.	Amyl acetate.	Amyl butyrate.	Amyl valerianate.	Essence of orange.	Cold saturated alcoholic solution of: Tartaric acid.	Oxalic acid.	Succinic acid.	Benzoic acid.
Pineapple	3	1	..	1	..	.	5	..	..	..	..	..	..	10	..	..	..	..	..	..
Melon	3	..	..	2	..	1	4	5	..	..	10	..	..	..	..	..	..	..	.	..
Strawberry	2	..	1	..	5	1	5	..	..	..	..	1	3	2	..	..	..	..	..	..
Raspberry	4	..	1	1	5	1	1	..	1	1	1	1	1	1	..	..	5	.	1	..
Gooseberry	..	..	..	1	5	..	..	..	1	1	..	..	..	..	..	..	5	..	1	1
Grape	10	2	..	2	..	2	..	..	..	10	..	1	..	..	..	..	5	..	3	..
Apple	4	1	1	2	1	.	..	..	..	..	..	..	..	..	10	..	..	1	..	..
Orange	10	2	..	2	5	1	1	..	1	..	..	1	10	..	..	10	1	..	..	..
Pear	10	..	..	..	5	..	..	..	..	..	..	..	10	..	..	..	..	..	..	..
Lemon	5	1	1	2	10	..	..	..	..	..	..	..	..	..	10	..	10	..	1	..
Wild cherry	..	..	..	..	10	..	..	..	5	2	..	..	..	..	..	..	..	1	..	2
Cherry	3	..	..	..	5	..	..	..	5	1	..	..	..	..	..	..	..	..	.	1
Plum	8	..	..	5	5	1	2	..	..	4	..	..	..	..	..	..	..	..	..	..
Apricot	4	1	..	..	..	..	10	5	..	1	..	2	..	1	..	..	1	..	..	..
Peach	5	..	..	2	5	5	5	5	..	5	1	2	..	..	..	..	..	..	..	..

The figures indicate the number of cubic centimetres to be added to 100 c.c. of alcohol.

Other mixtures of ethers of the same class are used in the manufacture of imitation spirits. Ethyl formiate predominates in *essence of rum*, and ethyl pelargonate in *essence of cognac*.

Ethyl carbonates are two in number: $\left.\begin{matrix}CO\\C_2H_5\\H\end{matrix}\right\}O_2$, ethyl-carbonic or carbovinic acid, and $\left.\begin{matrix}CO\\(C_2H_5)_2\end{matrix}\right\}O_2$, ethyl carbonate or carbonic ether. The former is a monobasic acid, the latter a neutral body. By the action of ammonia upon ethyl carbonate in the cold *ethyl carbonate* or *urethan*, $CO(NH_2)O,C_2H_5$, is formed; and under the influence of heat, *urea*, $CO(NH_2)_2$.

Ethyl oxalates.—Oxalic acid, being dibasic, forms two series of ethers; of ethylic ethers there are $C_2O_4(C_2H_5)H$, *ethyloxalic* or *oxalovinic* acid, and $C_2O_4(C_2H_5)_2$, *ethyl oxalate* or *oxalic ether*. The former is a monobasic acid, isomeric with succinic acid; the latter is neutral.

Amylic.

Amyl nitrate, $\left.\begin{matrix}NO_2\\C_5H_{11}\end{matrix}\right\}O$—is obtained by a process similar to that used for preparing the corresponding ethyl compound, by the distillation of a mixture of nitric acid and amylic alcohol in the presence of a small quantity of urea. It is a colorless, oily liquid; has an odor resembling

that of bed-bugs, and a sweetish, burning taste; sp. gr. 0.994 at 10°; boils at 148°, with partial decomposition.

Amyl nitrite—*Amyl nitrous ether*—$\left.\begin{matrix}NO\\C_5H_{11}\end{matrix}\right\}O$—prepared by directing the nitrous fumes, evolved by the action of nitric acid upon starch, into amyl alcohol contained in a retort heated over a water-bath, purifying the distillate by washing with an alkaline solution, and rectifying.

It is a slightly yellowish liquid; sp. gr. 0.877; boils at 95°; its vapor explodes when heated to 260°; insoluble in water; soluble in alcohol in all proportions; vapor orange-colored.

Alcoholic solution of potash decomposes it slowly, with formation of potassium nitrite and oxides of ethyl and amyl. When dropped upon fused potash, it ignites and yields potassium valerianate.

Amyl nitrite is frequently impure; its boiling-point should not vary more than two or three degrees from that given above.

Amyl sulphates—Are the same in constitution as those of ethyl, and are obtained by similar methods. *Amyl sulphuric acid* is of historical interest, as it was by its formation that Williamson showed the true nature of the process of etherification. The amyl sulphate of barium, prepared from *active* amyl alcohol, is three times more soluble than that made from the *inactive*—a property which is utilized to separate the two alcohols.

Amyl acetate, $\left.\begin{matrix}C_2H_3O\\C_5H_{11}\end{matrix}\right\}O$—Obtained by distilling a mixture of amyl alcohol, potassium acetate, and sulphuric acid. A limpid, colorless liquid; sp. gr. 0.8762; boils at 125°; insoluble in water; soluble in alcohol and ether. Its alcoholic solution is used as artificial pear-essence.

Of the great number of other ethers of this series, there are none of particular practical importance until we reach

Cetyl palmitate, $\left.\begin{matrix}C_{16}H_{31}O\\C_{16}H_{33}\end{matrix}\right\}O$—Also known as *cetine*, which is the chief constituent of *Spermaceti=cetaceum* (U. S., Br.). This is the concrete portion, obtained by expression and crystallization from alcohol, of the oil contained in the cranial sinuses of the sperm-whale. It forms white crystalline plates; fusible at 49°; slightly unctuous to the touch; tasteless, and almost odorless; insoluble in water; soluble in alcohol and ether; burns with a bright flame. It was formerly supposed to consist entirely of cetine, but recently it has been shown to contain ethers not only of palmitic, but also of stearic, myristic, and laurostearic acids; and of the alcohols: lethal, $C_{12}H_{26}O$; methal, $C_{14}H_{30}O$; ethal, $C_{16}H_{34}O$; and stethal, $C_{18}H_{38}O$.

Melissyl palmitate—*Melissin*—$\left.\begin{matrix}C_{16}H_{31}O\\C_{30}H_{61}\end{matrix}\right\}O$—*Beeswax*—*Cera flava* (U. S., Br.)—consists mainly of two substances: cerotic acid, which is soluble in boiling alcohol and melissyl palmitate, insoluble in that liquid, united with minute quantities of substances which communicate to the wax its color, odor, and unctuousness. Yellow wax melts at 62°—63°; after bleaching, which is brought about by exposure to light, air, and moisture, it does not fuse below 66°. *China wax*, a white substance resembling spermaceti, is a vegetable product consisting of *ceryl cerotate*, $C_{27}H_{55}O_2$ ($C_{27}H_{55}$).

ALDEHYDES.

SERIES $C_nH_{2n}O$.

Formic aldehyde.....CH_2O.	Valerianic aldehyde.....$C_5H_{10}O$.
Acetic aldehyde.....C_2H_4O.	Caproic aldehyde.....$C_6H_{12}O$.
Propionic aldehyde.....C_3H_6O.	Œnanthylic aldehyde.....$C_7H_{14}O$.
Butyric aldehyde.....C_4H_8O.	Caprylic aldehyde.....$C_8H_{16}O$.
Isobutyric aldehyde.....C_4H_8O.	Palmitic aldehyde.....$C_{16}H_{32}O$.

Acetic Aldehyde.

Acetyl hydride, $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}$.—Although discovered in 1821 by Doebereiner, and subsequently studied by Liebig, it is only of late years that the importance of this body in the organic laboratory has been recognized.

It is formed in all reactions in which alcohol is deprived of hydrogen without simultaneous introduction of oxygen; whence the name of "dehydrogenated alcohol." It is prepared by the process suggested by Liebig: a mixture of sulphuric acid, six parts; water, four parts; alcohol, four parts, powdered manganese dioxide, six parts, is placed in a capacious retort, which is connected with a receiver cooled by a freezing mixture; the retort is warmed very slowly and gently. The distillate, which is a mixture of water, alcohol, ether, aldehyde, and other substances, is redistilled from calcium chloride at a temperature not exceeding 50°. This second distillate is mixed with two volumes of ether, cooled by a freezing mixture, and saturated with dry ammonia gas; there separate fine, colorless crystals of ammonium acetylide, having the composition C_2H_3O,NH_4, which are washed with ether and dried by exposure to dry air; they are placed in a retort over the water-bath and decomposed by the addition of the proper quantity of dilute sulphuric acid; a clear liquid distils over, which is dried by contact with fused calcium chloride, and rectified at a temperature not exceeding 35°.

As thus obtained, aldehyde is a colorless, mobile liquid; has a strong, suffocating odor; sp. gr. 0.790 at 18°; boils at 21°; soluble in all proportions in water, alcohol, and ether. If perfectly pure, it may be kept unchanged; but if an excess of acid have been used in its preparation, it gradually decomposes. When heated to 100°, it is decomposed into water and crotonic aldehyde.

In the presence of nascent hydrogen, aldehyde takes up H_2 and regenerates alcohol. Chlorine converts it into acetyl chloride, C_2H_3O, Cl, and other products. Oxidizing agents quickly convert it into acetic acid, $C_2H_4O_2$. Sulphuric, hydrochloric, and sulphurous acids at the ordinary temperature convert it into a solid substance called *paraldehyde*, $C_6H_{12}O_3$, (?), which fuses at 10.5°, boils at 124°, and is more soluble in cold than in warm water. When heated with potassium hydrate, aldehyde becomes brown, a brown resin separates, and the solution contains potassium formiate and acetate. Gaseous ammonia converts aldehyde into the crystalline *ammonium acetylide*, mentioned above. If a watery solution of aldehyde be treated, first with ammonia and then with hydrogen sulphide, a solid, crystalline base, *thialdine*, $C_6H_{13}NS_2$, separates. Aldehyde

also forms crystalline compounds with the alkaline bisulphites. It decomposes solutions of silver nitrate, separating the silver in the metallic form, and under conditions which cause it to adhere strongly to glass; a fact which is utilized in making certain glass-silvering solutions.

Vapor of aldehyde, when inhaled in a concentrated form, produces asphyxia, even in comparatively small quantity; when diluted with air it is said to act as an anæsthetic. When taken internally it causes sudden and deep intoxication, and it is to its presence that the first products of the distillation of spirits of inferior quality owe in a great measure their rapid, deleterious action.

Trichloraldehyde.

Trichloracetyl hydride; Chloral—$\left.\begin{matrix} C_2Cl_3O \\ H \end{matrix}\right\}$—discovered in 1832, by Liebig. It is one of the final products of the action of chlorine upon alcohol, and is obtained by passing dry chlorine through absolute alcohol to saturation; applying heat toward the end of the reaction, which requires several hours for its completion. The liquid separates into two layers: the lower is removed and shaken with an equal volume of concentrated sulphuric acid and again allowed to separate into two layers; the upper is decanted; again mixed with sulphuric acid, from which it is distilled; the distillate is treated with quicklime, from which it is again distilled, that portion which passes over between 94° and 99° being collected. It sometimes happens that chloral in contact with sulphuric acid is converted into a modification, insoluble in water, known as *metachloral;* when this occurs it is washed with water, dried and heated to 180°, when it is converted into the soluble variety, which distils over.

Chloral is a colorless liquid, unctuous to the touch; has a penetrating odor and an acrid, caustic taste; sp. gr. 1.502 at 18°; boils at 94.4°; very soluble in water, alcohol, and ether; dissolves chlorine, bromine, iodine, sulphur, and phosphorus; its vapor is highly irritating; it distils without alteration.

The metachloral mentioned above is a white, volatile solid, having an ethereal odor; insoluble in water, alcohol, and ether; convertible at 180° into the liquid chloral, with which it is identical in chemical properties.

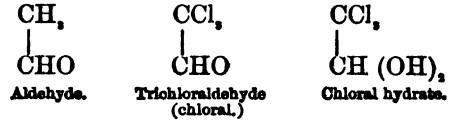
Although chloral has not been obtained by the direct substitution of chlorine for hydrogen in aldehyde, its reactions show it to be an aldehyde; it forms crystalline compounds with the bisulphites; it reduces solutions of silver nitrate in the presence of ammonia; ammonia and hydrogen sulphide form with it a compound similar to thialdine; with nascent hydrogen it regenerates aldehyde; oxidizing agents convert it into trichloracetic acid.

Alkaline solutions decompose chloral with formation of chloroform and a formiate:

$$\underset{\text{Chloral.}}{C_2HCl_3O} + \underset{\substack{\text{Potassium}\\ \text{hydrate.}}}{KHO} = \underset{\text{Chloroform.}}{CHCl_3} + \underset{\substack{\text{Potassium}\\ \text{formiate.}}}{CHO_2K}$$

With a small quantity of water, chloral forms a solid, crystalline hydrate, heat being at the same time liberated. This hydrate has the com-

position C_2HCl_3O,H_2O, and its constitution, as well as that of chloral itself, is indicated by the formulæ:



Chloral hydrate is a white, crystalline solid; fuses at 57°; boils at 98°, at which temperature it suffers partial decomposition into chloral and water; volatilizes slowly at ordinary temperatures; is very soluble in water; neutral in reaction; has an ethereal odor, and a sharp, pungent taste. Concentrated sulphuric acid decomposes it with formation of chloral and *chloralide*. Nitric acid converts it into trichloracetic acid. When pure it gives no precipitate with silver nitrate solution, and is not browned by contact with concentrated sulphuric acid.

Chloral also combines with alcohol, with elevation of temperature, to form a solid, crystalline body—*chloral alcoholate*.

$$CCl_3-CH\begin{matrix}OH\\ O-C_2H_5\end{matrix}.$$

Action of chloral hydrate upon the economy.—Although it was the ready decomposition of chloral into a formiate and chloroform which first suggested its use as a hypnotic to Liebreich, and although this decomposition was at one time believed to occur in the body under the influence of the alkaline reaction of the blood, more recent investigations have shown that the formation of chloroform from chloral in the blood is, to say the least, highly improbable, and that chloral has, in common with many other chlorinated derivatives of this series, the property of acting directly upon the nerve-centres.

Neither the urine nor the expired air contain chloroform when chloral is taken internally; when taken in large doses, chloral appears in the urine. The fact that the action of chloral is prolonged for a longer period than that of the other chlorinated derivatives of the fatty series is probably due, in a great measure, to its less volatility and less rapid elimination.

When taken in overdose, chloral acts as a poison, and its use as such is rapidly increasing as acquaintance with its powers becomes more widely disseminated.

No chemical antidote is known; the treatment should be directed to the removal of any chloral remaining in the stomach by the stomach-pump, and to the maintenance or restoration of respiration.

In fatal cases of poisoning by chloral that substance may be detected in the blood, urine, and contents of the stomach by the following method: the liquid is rendered strongly alkaline with potassium hydrate; placed in a flask, which is warmed to 50°—60°, and through which a slow current of air, heated to the same temperature, is made to pass; the air, after bubbling through the liquid, is tested for chloroform by the methods described on p. 165. If affirmative results are obtained in this testing, it remains to determine whether the chloroform detected existed in the fluid tested in its own form, or resulted from the decomposition of chloral; to this end a fresh portion of the suspected liquid is *rendered acid* and tested by Hofmann's method, (p. 165); if chloroform be present, the char-

acteristic odor of isobenzonitril is observed, while chloral, not being decomposed in acid solution, gives a negative result. The nitrate of silver test is not available for this purpose in liquids containing chlorides, as these, in the presence of even the weakest acids, are partially decomposed with liberation of hydrochloric acid.

The corresponding bromine and iodine compounds are also known.

Bromal, $\begin{matrix}CBr_3\\|\\CHO\end{matrix}$—a colorless, oily liquid; sp. gr. 3.34; boils at 172°; has a persistent, sharp, burning taste, and a penetrating odor; its vapor irritates the air-passages and eyes; neutral; soluble in water, alcohol, and ether. By union with water it forms *bromal hydrate,* $\begin{matrix}CBr_3\\|\\CH(OH)_2\end{matrix}$; large, colorless, transparent crystals; fusible at the temperature of the body; soluble in water; has the same taste and odor as bromal; decomposed by alkalies into bromoform and a formiate. Produces anæsthesia without sleep; very poisonous.

Iodal and its hydrate have also been obtained.

The higher aldehydes of this series are obtainable from the corresponding acids by distilling a mixture of calcium formiate and the calcium salt of the corresponding acid:

$$\underset{\text{Calcium formiate.}}{(CHO_2)_2Ca} + \underset{\text{Calcium butyrate.}}{(C_4H_7O_2)_2Ca} = \underset{\text{Calcium carbonate.}}{2CO_3Ca} + \underset{\text{Butyric aldehyde.}}{2C_4H_8O}$$

As with the acids and alcohols, there exist isomeres of the aldehydes above propylic aldehyde; such are *butyral* and *valeral. Caprylic aldehyde,* $C_8H_{16}O$ is one of the products of decomposition of the fatty oils at high temperatures, and, together with acrolein (*q. v.*), produces the unpleasant and deleterious odor observed in engine-rooms, especially on shipboard.

KETONES OR ACETONES.

Series $C_nH_{2n}O$.

Dimethyl ketone, $CO\begin{matrix}CH_3\\CH_3\end{matrix}$*—Acetone—Acetyl methylide—Pyroacetic ether—Pyroacetic spirit*—is formed as one of the products of the dry distillation of the acetates; by the decomposition of the vapor of acetic acid at a red heat; by the dry distillation of sugar, tartaric acid, etc.; and in a number of other reactions. It is obtained by distilling dry calcium acetate in an earthenware retort at a dull red heat; the distillate, collected in a well-cooled receiver, is freed from water by digestion with fused calcium chloride, and rectified; those portions being collected which pass over at 60°. It is also formed in large quantity in the preparation of aniline, when that substance is distilled with acetate of iron.

It is a limpid, colorless liquid; sp. gr. 0.7921 at 18°; boils at 56°; soluble in water, alcohol, and ether, has a peculiar, ethereal odor, and a burning taste; is a good solvent of resins, fats, camphor, gun-cotton; readily inflammable.

It forms crystalline compounds with the alkaline bisulphites. Chlorine and bromine, in the presence of alkalies, convert it into chloroform or bromoform; chlorine alone produces with acetone a number of chlorinated products of substitution. Certain oxidizing agents transform it into a mixture of formic and acetic acids; others into oxalic acid.

Acetone has been found to exist in the blood and urine in certain pathological conditions, and notably in diabetes; the peculiar odor exhaled by diabetics is produced by this substance, which has also been considered by some authors as being the cause of the respiratory derangements and coma which frequently occur in the last stages of the disease.

That acetone exists in the blood in such cases is certain; it is not certain, however, that its presence produces the condition designated as *acetonæmia*. It can hardly be doubted that the acetone thus existing in the blood is indirectly formed from diabetic sugar, and it is probable also that a complex acid, known as *ethyldiacetic*, is formed as an intermediate product, and gives rise to acetone by the reaction:

$$\underset{\text{Sodium ethyl-diacetate.}}{C_6H_9O_3Na} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Acetone.}}{C_3H_6O} + \underset{\text{Alcohol.}}{C_2H_6O} + \underset{\text{Hydrosodic carbonate.}}{CO_3HNa}$$

The higher ketones of this series, *propione*, *butyrone*, etc., are obtained by similar methods, from the calcium salts of the corresponding acids. Their interest is purely theoretical.

MONAMINES.

General methods of preparation.—The *primary* monamines are formed by the action of potassium hydrate upon the corresponding cyanic ether:

$$\underset{\text{Ethyl cyanate.}}{CNO,C_2H_5} + \underset{\text{Potash.}}{2KHO} = \underset{\text{Ethylamine.}}{NH_2,C_2H_5} + \underset{\text{Potassium carbonate.}}{CO_3K_2}$$

Or by heating together an alcoholic solution of ammonia and an ether:

$$\underset{\text{Ethyl iodide.}}{C_2H_5I} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Hydriodic acid.}}{HI} + \underset{\text{Ethylamine.}}{NH_2,C_2H_5}$$

Or by the action of nascent hydrogen upon the cyanides of the alcoholic radicals:

$$\underset{\text{Methyl cyanide.}}{CN,CH_3} + \underset{\text{Hydrogen.}}{2H_2} = \underset{\text{Ethylamine.}}{NH_2,C_2H_5}.$$

The *secondary* monamines are formed by the action of the iodides or bromides of the alcoholic radicals upon the primary monamines.

The *tertiary* monamines are produced by the distillation of the hydrates or iodides of the quaternary ammoniums, or by the action of the iodides of the alcoholic radicals upon the secondary monamines.

General properties.—The amines of this series, containing radicals of monoatomic alcohols, have the same power of saturation as ammonia.

They are volatile. The alkalinity and solubility in water of the primary monamines are greater than those of the secondary, and those of the secondary greater than those of the tertiary. Their chlorides form sparingly soluble compounds with platinic chloride, similar to that formed with the same salt by ammonium chloride. Nitrous acid decomposes the monamines, with regeneration of the corresponding alcohol:

$$\underset{\text{Ethylamine.}}{NH_2,C_2H_5} + \underset{\text{Nitrous acid.}}{NO_2H} = \underset{\text{Ethylic alcohol.}}{C_2H_5HO} + \underset{\text{Water.}}{H_2O} + \underset{\text{Nitrogen.}}{N_2}.$$

With the secondary and tertiary monamines the same reagent produces *nitroso*-compounds, in which an atom of hydrogen is replaced by the group (NO)′.

The three classes of monamines may be separated by the action of ethyl oxalate, which forms with the primary a solid compound, and with the secondary a liquid, while the tertiary remains free.

There are but few of the monamines of this series which are of practical importance.

Methylamine—*Methylia*—$\left.\begin{matrix}CH_3\\H_2\end{matrix}\right\}N$—is obtained by decomposing methyl cyanate by potash, and directing the vapors through dilute hydrochloric acid; the methyl ammonium chloride thus obtained is decomposed by quicklime, and the methylamine collected over mercury.

It is a colorless gas; has a fishy, ammoniacal odor; liquefies a few degrees below 0°; inflammable; is the most soluble gas known; one volume of water dissolves 1,154 volumes of methylamine at 12.5°, and 959 volumes at 25°; its solution is strongly alkaline and caustic, and has the odor of the gas. Its salts are soluble in boiling alcohol. In solution it is distinguishable from ammonia and from ethylamine by its failure to form a precipitate with protochloride of molybdenum, and by the formation of a reddish precipitate, insoluble in excess, with molybdenum bichloride. Its chloroplatinate is yellow, and soluble in boiling water.

Dimethylamine—*Dimethylia*—$\left.\begin{matrix}(CH_3)_2\\H\end{matrix}\right\}N$—is a liquid below 8°, at which temperature it boils; has an ammoniacal odor; is quite soluble in water; is formed by the action of methyl iodide on ammonia.

Trimethylamine—*Trimethylia*—$(CH_3)_3N$—is formed with methylamine and dimethylamine, by the action of methyl iodide upon ammonia, by the series of reactions;

$$\begin{aligned} H_3N + CH_3I &= (CH_3)H_2N + HI.\\ (CH_3)H_2N + CH_3I &= (CH_3)_2HN + HI.\\ (CH_3)_2HN + CH_3I &= (CH_3)_3N + HI. \end{aligned}$$

It is also formed as a product of decomposition of many organic substances, and exists widely disseminated in nature. It is one of the products of the action of potash on many vegetable substances, alkaloids, etc., of the putrefaction of fish and starch-paste; it occurs in cod-liver-oil, in ergot, in chenopodium, in the flowers of many plants, in yeast, in guano, in herring-pickle, in human urine, and in the blood of the calf. It is usually obtained by distillation from the pickle in which fish has been preserved.

At temperatures below its boiling-point, 9°, it is an oily liquid, having

a disagreeable odor of spoiled fish; alkaline; soluble in water, alcohol, and ether; inflammable. It combines with acids to form salts of trimethylammonium, which are crystallizable.

It has frequently been mistaken by writers upon materia medica for its isomere *propylamine*, $\left.\begin{matrix}(C_3H_7)\\H_2\end{matrix}\right\}N$, which differs from it in odor and in boiling at 50°. Its chloride, under the names *chloride of propylamia, of secalia, of secalin*, has been used in the treatment of gout and of rheumatism.

Tetramethyl ammonium hydrate—$(CH_3)_4N,OH$.—This substance, whose constitution is similar to that of ammonium hydrate, is obtained by decomposing the corresponding iodide, $(CH_3)_4NI$, formed by the action of methyl iodide upon trimethylamine. It is a crystalline solid, deliquescent, very soluble in water; caustic; not volatile without decomposition; it attracts carbon dioxide from the air, and combines with acids to form crystallizable salts.

The iodide is said to exert an action upon the economy similar to that of curare.

Ethylamine—*Ethylia*—$\left.\begin{matrix}(C_2H_5)\\H_2\end{matrix}\right\}N$—is obtained by the action of potash upon ethyl cyanate. It is a light, colorless, mobile liquid; boils at 18.7°; has a strong odor like that of ammonia; burns with a bluish flame; soluble in all proportions in water, alcohol, and ether. It expels ammonia from its salts, combining itself with the acid; its salts are for the most part crystallizable, and are soluble in absolute alcohol. With chlorine, bromine, and iodine it forms products of substitution containing two atoms of the halogen. It forms precipitates in solutions of most of the metallic salts, and behaves like ammonia with solutions of cupric salts. The precipitate which it forms in solutions of the alumina salts is soluble in an excess of ethylamine.

Diethylamine—*Diethylia*—$\left.\begin{matrix}(C_2H_5)_2\\H\end{matrix}\right\}N$—is an inflammable, colorless liquid, very soluble in water; boiling at 57°; having an ammoniacal odor, and resembling ethylamine in most of its reactions.

Triethylamine—*Triethylia*—$(C_2H_5)_3N$—is a colorless liquid, lighter than water, in which it is sparingly soluble; boiling at 91°; having an ammoniacal odor and an alkaline reaction.

Tetrethyl ammonium hydrate, $(C_2H_5)_4N,OH$—is a crystalline solid, very deliquescent; soluble in water, and powerfully basic.

Choline; neurine, $\left.\begin{matrix}(CH_3)_3\\(C_2H_4,OH)\end{matrix}\right\}N,OH$.—This interesting compound is a quaternary monammonium hydrate, containing three methyl groups, and one ethylene hydroxide group. It has not as yet been found to exist free in the animal body, but only as a constituent of those important elements of nerve-tissue, the *lecithins* (*q. v.*). It was first obtained from bile, but is best prepared from the yolks of eggs.

It appears as a thick syrup, soluble in water and in alcohol, and strongly alkaline in reaction. Even in dilute aqueous solution it prevents the coagulation of albumin and redissolves coagulated albumin and fibrin. It is a strong base; attracts carbon dioxide from the air; forms with hydrochloric acid a salt, soluble in alcohol, which crystallizes in plates and needles, very much resembling in appearance those of cholesterin.

Choline has been obtained synthetically by the action of a concen-

trated solution of trimethylamine upon ethylene oxide, or upon ethylene chlorhydrate. When heated, it splits up into glycol and trimethylamine.

By partial oxidation a solid, crystalline base, known as *oxyneurine*, *oxycholine*, or *betaïn*, is formed; in this substance, which has also been obtained by synthesis, the group C_2H_4OH is replaced by C_2H_3O,OH.

Choline is isomeric with *amanitine*, and betaïn with *muscarine;* poisonous alkaloids obtained from species of *Agaricus*.

Besides the amines here considered, many containing the higher alcoholic radicals have been obtained. There are also amines containing two or more different alcoholic radicals, such as *methyl-ethyl-amylamine*, $\left.\begin{matrix}CH_3\\C_2H_5\\C_5H_{11}\end{matrix}\right\}N$.

MONAMIDES.

General methods of preparation.—The *primary* monamides, containing radicals of the acids of the acetic series, are formed:

First.—By the action of heat upon an ammoniacal salt:

$$\left.\begin{matrix}(C_2H_3O)'\\NH_4\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N$$

Ammonium acetate. Water. Acetamide.

Second.—By the action of a compound ether upon ammonia:

$$\left.\begin{matrix}(C_2H_3O)'\\(C_2H_5)'\end{matrix}\right\}O + \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N = \left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$$

Ethyl acetate. Ammonia. Acetamide. Alcohol.

Third.—By the action of the chloride of an acid radical upon dry ammonia:

$$\left.\begin{matrix}(C_2H_3O)'\\Cl\end{matrix}\right\} + 2\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right) = \left.\begin{matrix}NH_4\\Cl\end{matrix}\right\} + \left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N$$

Acetyl chloride. Ammonia. Ammonium chloride. Acetamide.

The *secondary* monamides of the same class are obtained: *First*, by the action of the chlorides of acid radicals upon the primary amides:

$$\left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N + \left.\begin{matrix}(C_2H_3O)'\\Cl\end{matrix}\right\} = \left.\begin{matrix}(C_2H_3O)_2\\H\end{matrix}\right\}N + \left.\begin{matrix}H\\Cl\end{matrix}\right\}$$

Acetamide. Acetyl chloride. Diacetamide. Hydrochloric acid.

Second.—By the action of hydrochloric acid upon the primary monamides at high temperatures:

$$2\left(\left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N\right) + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = \left.\begin{matrix}(C_2H_3O)_2\\H\end{matrix}\right\}N + \left.\begin{matrix}NH_4\\Cl\end{matrix}\right\}$$

Acetamide. Hydrochloric acid. Diacetamide. Ammonium chloride.

The *tertiary* monamides of this series of radicals have been but imperfectly studied; some of them have been obtained by the action of the chlorides of acid radicals upon metallic derivatives of the secondary amides.

General properties.—The *primary* monamides containing radicals of the fatty acids are solid, crystallizable, neutral in reaction, volatile without decomposition, mostly soluble in alcohol and ether, and mostly capable of uniting with acids to form compounds similar in constitution to the ammoniacal salts. They are capable of uniting with water to form the ammoniacal salt of the corresponding acid, and with the alkaline hydrates to form the metallic salt of the corresponding acid, and ammonia. The *secondary* monamides, containing two radicals of the fatty series, are acid in reaction, and their remaining atom of extra-radical hydrogen may be replaced by an electro-positive atom.

Formamide, $\left.\begin{matrix}(CHO)\\H_2\end{matrix}\right\}N$—is a colorless liquid; soluble in water and in alcohol; boils at 192°; formed by the action of ethyl formiate upon dry ammonia.

Acetamide, $\left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N$—is obtained by heating, under pressure, a mixture of ethyl acetate and aqua ammoniæ, and purifying by distillation. It is a solid, crystalline substance, very soluble in water, alcohol, and ether; fuses at 78°; boils at 221°; has a sweetish, cooling taste, and an odor of mice. Boiling potassium hydrate solution decomposes it into potassium acetate and ammonia. Phosphoric anhydride deprives it of the elements of water, and forms with it *acetonitrile* or *methyl cyanide.*

There exist also amides corresponding to *monochloracetic* and *trichloracetic* acids.

AMIDO-ACIDS OF THE FATTY SERIES.

Amido-acetic acid—*Glycocol—Sugar of gelatin—Glycolamic acid—Glycine*—$\begin{matrix}CH_2,NH_2\\|\\COOH\end{matrix}$.—This interesting body was first obtained by the action of sulphuric acid upon gelatin. It is best prepared by acting upon glue with caustic potassa, ammonia being liberated; sulphuric acid is then added, and the crystals of potassium sulphate separated; the liquid is evaporated, the residue dissolved in alcohol, from which solution the glycocol is allowed to crystallize.

It may also be obtained synthetically by a method which indicates its constitution—by the action of ammonia upon chloracetic acid.

$$\underset{\text{Chloracetic acid.}}{\begin{matrix}CH_2Cl\\|\\COOH\end{matrix}} + \underset{\text{Ammonia.}}{\begin{matrix}H\diagdown\\H—N\\H\diagup\end{matrix}} = \underset{\text{Amidoacetic acid.}}{\begin{matrix}CH_2NH_2\\|\\COOH\end{matrix}} + \underset{\text{Hydrochloric acid.}}{\begin{matrix}H\\Cl\end{matrix}}$$

It may be obtained from ox-bile, in which it exists as the salt of a conjugate acid; from uric acid by the action of hydriodic acid; and by the union of formic aldehyde, hydrocyanic acid, and water. It is isomeric with *glycolamide.*

It has been found to exist free in animal nature only in the muscle of the scallop, and, when taken internally, its constituents are eliminated as urea. In combination it exists in the gelatinoids, and with cholic acid as sodium glycocholate (*q. v.*) in the bile; it is one of the products of decomposition of glycocholic acid, hyoglycocholic acid, and hippuric acid by dilute acids and by alkalies, and of the decomposition of tissues containing gelatinoids.

It appears as large, colorless, transparent crystals; has a sweet taste; melts at 170°; decomposes at higher temperatures; sparingly soluble in cold water; much more soluble in warm water; insoluble in absolute alcohol and in ether; acid in reaction.

It combines with acids to form crystalline compounds, which are decomposed at the temperature of boiling water; hot sulphuric acid carbonizes it; nitric acid converts it into glycolic acid (*q. v.*); with hydrochloric acid it forms a chloride; heated under pressure with benzoic acid it forms hippuric acid. Its acid function is more marked; it expels carbonic and acetic acids from calcium carbonate and plumbic acetate. The presence of a small quantity of glycocol prevents the precipitation of cupric hydrate from cupric sulphate solution by potassium hydrate; the solution becomes dark blue, does not yield cuprous hydrate on boiling, and precipitates crystalline needles of copper glycolamate on the addition of alcohol to the cold solution. With ferric chloride it gives an intense red solution, whose color is discharged by acids, and reappears on neutralization. With phenol and sodium hypochlorite it gives a blue color, as does ammonia. By oxidation with potassium permanganate in alkaline solution it yields carbon dioxide, oxalic, carbonic, and oxamic acids, and water. It also forms crystalline compounds, with many salts and ethers. Methyl glycolamate is isomeric with sarcosine:

CH_2NH_2	CH_2NH_2	$CH_2NH(CH_3)$
$COOH$	$COOCH_3$	$COOH$
Glycocol (amido-acetic acid).	Methyl-glycolamate.	Sarcosine (methyl-glycocol).

Methyl-glycocol—*Sarcosine* $CH_2[NH(CH_3)]$ $COOH$ —This substance, which is isomeric with alanine and with lactamide (*q. v.*), does not exist as such in animal nature, but has been obtained from creatine (*q. v.*) by the action of barium hydrate:

$C_4H_9N_3O_2$	+	H_2O	=	$C_3H_7NO_2$	+	CON_2H_4
Creatine.		Water.		Sarcosine.		Urea.

Urea being formed at the same time, and decomposed by the further action of the barium hydrate into ammonia and barium carbonate.

Its constitution is indicated by its synthetic formation from chloracetic acid and methylamine:

CH_2Cl		CH_3		$CH_2[NH(CH_3)]$		H
$COOH$	+	$H—N$	=	$COOH$	+	Cl
		H				
Chloracetic acid.		Methylamine.		Sarcosine.		Hydrochloric acid.

It crystallizes in colorless, transparent prisms; very soluble in water; sparingly soluble in alcohol and ether. Its aqueous solution is not acid, and has a sweetish taste; it unites with acids to form crystalline salts, but does not form metallic salts. It is capable of combining with cyanamide to form creatine.

Biliary Acids.

The bile of most animals contains the sodium salts of two amido-acids of complex constitution. These acids may be decomposed into a non-nitrogenized acid (cholic acid), and either an amido-acid (glycocol), or an amido-sulphurous acid (taurine). The following biliary acids have been described:

Glycocholic acid, $C_{26}H_{43}NO_6$—(sometimes designated as *Acide cholique*, *Cholsäure*, *Cholic acid*, especially by French and German writers, who retain the names given it by Gmelin, but which had been previously applied to another substance by Demarçay.) It exists as its sodium salt in the bile of the herbivora, and in much smaller proportion in that of the carnivora; it exists in small quantity in human blood and urine in icterus; in human bile its quantity varies with the diet.

It is best obtained from ox-bile; this is evaporated to one-fourth of its original volume, the residue is ground up with animal charcoal, and dried at 100°; the dry mass, while still hot, is broken up and introduced into a flask, in which it is digested with absolute alcohol, with repeated agitation for some days; the colorless, filtered alcoholic solution is partially evaporated, but not to the extent of becoming syrupy, then mixed with an excess of anhydrous ether, which, if the reagents were free from water, causes the immediate separation of a crystalline precipitate of the mixed biliary salts. If the alcohol or ether used contain water, the precipitate is at first resinous and only becomes crystalline after standing, or does not become crystalline if the proportion of water be too great. The crystalline deposit is collected upon a filter, washed with ether and dissolved in a small quantity of water; to the aqueous solution a small quantity of ether is added, and then enough dilute sulphuric acid to render the mixture permanently cloudy; the glycocholic acid gradually crystallizes out, and may be further purified by solution in alcohol, and precipitation with a great excess of ether.

Glycocholic acid forms brilliant, colorless, transparent needles, which are sparingly soluble in cold water, readily soluble in warm water and in alcohol, almost insoluble in ether. The watery solution is acid in reaction, and tastes at first sweet, afterward intensely bitter; its alcoholic solution exerts a right-handed polarization $[a]_D = +29°$; when evaporated it leaves the acid in a resinous form.

When heated with potash, baryta, or dilute sulphuric or hydrochloric acid, it is decomposed into *cholic acid* and glycocol:

$$\underset{\text{Glycocholic acid.}}{C_{26}H_{43}NO_6} + \underset{\text{Water.}}{H_2O} = \underset{\text{Cholic acid.}}{C_{24}H_{40}O_5} + \underset{\text{Glycocol.}}{C_2H_5NO_2}.$$

Glycocholic acid dissolves unchanged in cold concentrated sulphuric acid, and is precipitated on dilution of the solution with water; if the mixture be warmed the bile acid is decomposed, and there separate oily

drops of *cholonic acid*, $C_{26}H_{41}NO_5$, an acid substance, differing from glycocholic acid by $-H_2O$. When allowed to remain long in contact with concentrated sulphuric acid, glycocholic acid is converted into a colorless, resinous mass, which slowly forms a saffron-yellow solution with the mineral acid, which turns flame-red when warmed, and which, on dilution, deposits a flocculent material which is colorless, greenish, or brownish, according to the temperature at which it is formed. Glycocholic acid, altered by contact with concentrated sulphuric acid, absorbs oxygen when exposed to the air, and turns red, then blue, and finally brown after a few days.

Of the salts of glycocholic acid, *sodium glycocholate*, $C_{26}H_{42}NO_6Na$, exists in the bile; it crystallizes in stellate needles, very soluble in water, less so in absolute alcohol, and insoluble in ether; its alcoholic solution exerts right-handed polarization $[a]_D = +25.7°$.

Lead glycocholate, $(C_{26}H_{42}NO_6)_2Pb$ (?)—is formed as a white, flocculent precipitate, when solution of lead subacetate is added to a solution of a glycocholate or of glycocholic acid; with the *neutral* acetate the precipitation does not occur in the presence of an excess of acetic acid. It is soluble in alcohol, and in an excess of lead acetate solution.

The glycocholates of the alkaline earths are soluble in water. Glycocholic acid and the glycocholates react with Pettenkofer's test (see below).

Glycocholic acid forms compounds with the alkaloids, some of which are crystalline, others amorphous; they are for the most part very sparingly soluble in water, but readily soluble in solutions of the biliary salts and in bile.

Taurocholic acid, $C_{26}H_{45}NO_7S$ (called by Strecker *choleic acid*), exists as its sodium salt in the bile of man and of the carnivora, and in much less abundance in that of the herbivora; in the bile of the dog it seems to be unaccompanied by any other biliary acid. It may be obtained from dog's bile by a modification of the method described under glycocholic acid; the watery solution is not treated with sulphuric acid, as in the preparation of that acid, but with solution of basic lead acetate and ammonia. The precipitate so formed is extracted with boiling alcohol, the solution filtered hot and treated with hydrogen sulphide; the clear liquid, filtered from the precipitated lead sulphide, is evaporated to a small bulk and treated with a large excess of ether; the acid is precipitated in the resinous form, but, after standing for a varying period, assumes the crystalline form.

When carefully prepared it forms silky, crystalline needles, which, when exposed to the air, deliquesce rapidly, and which, even under absolute ether, are gradually converted into a transparent, amorphous, resinous mass. It is soluble in water and in alcohol, insoluble in ether; its aqueous solution is very bitter; in alcholic solution it deviates the plane of polarization to the right, $[a]_D = 24.5°$; its solutions are acid in reaction.

Taurocholic acid is very readily decomposed by heating with barium hydrate, with dilute acids, and even by evaporation of its solution, into cholic acid and *taurine*.

$$\underset{\text{Taurocholic acid.}}{C_{26}H_{45}NO_7S} + \underset{\text{Water.}}{H_2O} = \underset{\text{Cholic acid.}}{C_{24}H_{40}O_5} + \underset{\text{Taurine.}}{C_2H_7NO_3S}$$

The same decomposition occurs in the presence of putrefying material and in the intestine. Taurocholic acid has not been found to accompany glycocholic in the urine of icteric patients.

The taurocholates are neutral in reaction; those of the alkaline metals are soluble in alcohol and in water; and by long contact with ether they assume the crystalline form. They may be separated from the glycocholates in watery solution, either: 1st, by dilute sulphuric acid in the presence of a small quantity of ether, which precipitates glycocholic acid alone; or 2d, by adding *neutral* lead acetate to the solution of the mixed salts, which must be neutral in reaction, lead glycocholate is precipitated and separated by filtration; to the mother liquor basic lead acetate and ammonia are added, when lead taurocholate is precipitated. The acids are obtained from the hot alcoholic solutions of the lead salts by decomposition with hydrogen sulphide, filtration, concentration, and precipitation by ether.

Solutions of the taurocholates, like those of the glycocholates, have the power of dissolving cholesterin and of emulsifying the fats; they also form with the salts of the alkaloids compounds which are insoluble in water, but soluble in an excess of the biliary salt. The taurocholate of morphine is crystallizable. They react with Pettenkofer's test.

Hyoglycocholic acid, $C_{27}H_{43}NO_5$ and *hyotaurocholic acid*, $C_{27}H_{45}NO_6S$ (?) are conjugate acids of *hyocholic acid*, $C_{25}H_{40}O_4$, and glycocol and taurine, which exist in the bile of the pig. *Chenotaurocholic acid*, a conjugate acid of taurine and *chenocholic acid*, $C_{27}H_{44}O_4$, is obtained from the bile of the goose.

Cholic acid, $C_{24}H_{40}O_5$ (called by Strecker, *cholalic acid*), is a product of decomposition of glyco- and taurocholic acids, obtained as indicated above. It also occurs, as the result of a similar decomposition, in the intestines and fæces of both herbivora and carnivora. It forms large, clear, deliquescent crystals; sparingly soluble in water, readily soluble in alcohol and ether; intensely bitter in taste, with a sweetish aftertaste; in alcoholic solution it is dextrogyric $[a]_D=35°$. The alkaline cholates are crystallizable and readily soluble in water, the others difficultly soluble. Cholic acid and the cholates respond to Pettenkofer's test.

By boiling with acids or by continued heating to 200°, cholic acid loses the elements of water, and is transformed into *dyslysin*, $C_{24}H_{38}O_2$, a neutral, resinous material, insoluble in water and alcohol, sparingly soluble in ether.

Tests for the biliary acids—The Pettenkofer reaction.—All of the biliary acids, and the cholic acid and dyslysin obtained by their decomposition, have the property of forming a yellow solution with concentrated sulphuric acid, the color of which rapidly increases in intensity, and which exhibits a green fluorescence. Their watery solutions also, when treated with a small quantity of cane-sugar and with concentrated sulphuric acid, so added that the mixture acquires a temperature of 70° but does not become heated much beyond that point, develop a beautiful cherry-red color, which gradually changes to dark reddish purple. Although this reaction is observed in the presence of very small quantities of the biliary acids, it loses its value, unless applied as directed below, from the fact that many other substances give the same reaction, either with sulphuric acid alone, or in the presence of cane-sugar. Among these substances are many which exist naturally in animal fluids, or which may be introduced with the food or as medicines; such are cholesterin, the albuminoids, lecithin, oleic acid, cerebrin, phenol, turpentine, tannic acid, salicylic acid, morphine, codeine, many oils and fats, cod-liver oil, etc. It has been suggested that a distinction could be made between the color produced by the Pettenkofer test with the biliary acids, and those pro-

duced by the same test with other substances, by spectroscopic observation; the test with biliary acids in watery solution exhibiting a single dark and broad absorption-band, extending from E to midway between D and E; the same test with the acids in alcoholic solution shows two bands, one similar to that already described, and a second narrower and fainter at F. But while this spectrum differs from those observed in the purple solutions obtained with many other bodies under similar conditions, it does not differ sufficiently from that obtained with the morphine salts and with other substances, to render it a safe method for controlling the test.

The following method of applying Pettenkofer's test to the urine and other fluids removes, we believe, every source of error. The urine, etc., is first evaporated to dryness at the temperature of the water-bath, a small quantity of coarse animal charcoal having been added; the residue is extracted with absolute alcohol, the alcoholic liquid filtered, partially evaporated, and treated with ten times its bulk of absolute ether; after standing an hour or two, any precipitate which may have formed is collected upon a small filter, washed with ether, and dissolved in a small quantity of water; this aqueous solution is placed in a test-tube, a drop or two of a strong aqueous solution of cane-sugar (sugar, 1; water, 4), and then pure concentrated sulphuric acid, are added; the addition of the acid being so regulated, and the test-tube dipped from time to time in cold water, that the temperature shall be from 60°—75°. In the presence of biliary acids the mixture usually becomes turbid at first, and then turns cherry-red and finally purple, the intensity of the color varying with the amount of biliary acid present.

Physiological chemistry of the biliary acids.—That these substances do not normally pre-exist in the blood, and are consequently formed in the liver, and that they are not reabsorbed from the intestine unchanged, is shown by the experiments of Kunde, Moleschott, and Feltz and Ritter. The last-named have found that solutions of the biliary salts, injected into the circulation in small quantity, cause a diminution in the frequency of the pulse and of the respiratory movements, a lowering of the temperature and arterial tension, and disintegration of the blood-corpuscles; in large doses (2—4 grams for a dog) they produce the same effects to a more marked degree; epileptiform convulsions, black and bloody urine, and death, more or less rapidly. These effects do not follow the injection of the products of decomposition of the biliary acids, except cholic acid, and in that case the symptoms are much less well marked. Nor are the biliary acids discharged unaltered with the fæces; they are decomposed in the intestine. The extract, suitably purified, of the contents of the upper part of the small intestine, gives a well-marked reaction with Pettenkofer's test; while a similar extract of the contents of the lower part of the large intestine, or of the fæces, fail to give the reaction, and consequently are free from glyco- or taurocholic, cholic acid, or dyslysin; the fæces have, moreover, not been found to contain either taurine or glycocol. During the processes, at present but imperfectly understood, which take place in the intestine, the bile-acids are undoubtedly decomposed into cholic acid and taurine or glycocol, which are subsequently reabsorbed, either as such, or after having been subjected to further decomposition; and as a consequence of their decomposition they probably have some influence upon intestinal digestion.

The biliary salts are precipitated from their aqueous solution, or from bile, by fresh gastric juice from the same animal; but they are not so

precipitated if the gastric juice contain peptones. The proportion of biliary salts in human bile seems to vary considerably, as shown by the following analyses:

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Mucin	2.66	2.98	2.21	1.45	....	2.48	1.29	....	1.29
Cholesterin	0.16	0.26	4.73	3.09	0.25	0.25	0.34	....	0.35
Fats	0.32	0.92			0.04	0.05	0.36	....	0.73
Taurocholate of sodium, Glycocholate of sodium,	7.22	9.14	10.79	5.65	.... 4.48	0.75 2.09	1.93 0.44	1.57 4.90	0.87 3.03
Soaps	....	....	....	....	0.64	0.82	1.63	1.46	1.39
Mineral salts	0.65	0.77	1.08	0.63	3.86	0.46	1.46	....	....
Water	86.00	85.92	82.27	89.81	....	90.88	91.08	....	....
Total solids	14.00	14.08	17.73	10.19	....	9.12	8.92	....	....

I. Frerichs: Bile from man, æt. 18, killed by a fall. II. Frerichs: Male, æt. 22, died of a wound. III. Gorup-Besanez: Male, æt. 49, decapitated. IV. Gorup-Besanez: Female, æt. 29, decapitated. V. Jacobsen: Male, biliary fistula. VI., VII. Trifanowski: Males. VIII. Socoloff: Mean of six analyses of human bile. IX. Hoppe-Seyler: Mean of five analyses of bile from subjects with healthy livers.

Pathologically, the biliary acids may be detected in the blood and urine in icterus and acute atrophy of the liver, although by no means as frequently as the biliary coloring matters.

Amidopropionic Acid—*Alanine*, $\begin{matrix}CH_2—CH_2(NH_2)\\ |\\ COOH\end{matrix}$.—Isomeric with sarcosine and with lactamide; does not exist, so far as is known at present, in nature. It is obtained by the action of alcoholic ammonia upon bromoproprionic acid:

$$\begin{matrix}CH_2Br\\ |\\ CH_2\\ |\\ COOH\end{matrix} + 2\left(\begin{matrix}H\\ H—N\\ H\end{matrix}\right) = \begin{matrix}CH_2(NH_2)\\ |\\ CH_2\\ |\\ COOH\end{matrix} + BrNH_4.$$

Bromopropionic acid. Ammonia. Amidopropionic acid. Ammonium bromide.

It may also be prepared by starting from lactic acid, from which it differs by containing NH_2 in place of OH.

It crystallizes in large, oblique, rhombic prisms; very soluble in water; sparingly soluble in alcohol; insoluble in ether. Its aqueous solution is neutral and sweet. Nitrous acid converts it into lactic acid, nitrogen, and water. It dissolves in acids without neutralizing them, but yet, in certain cases, with the formation of crystalline compounds. Its barium, lead, copper, and silver salts are soluble and crystalline.

Amidobutyric Acid—*Butalanine*, $C_4H_9NO_2$, and **Amidovalerianic acid**, $C_5H_{11}NO_2$—are only of theoretic interest at present. The latter has been found in the tissue of the pancreas and among the products of the action of pancreatic juice upon albumin. They are both among the products of the decomposition of albumin by caustic baryta.

Amidocaproic Acid—*Leucine*—$\begin{matrix}CH_2—C_3H_6—CH_2(NH_2)\\ |\\ COOH\end{matrix} = C_6H_{13}NO_2$

—was first obtained by Proust as a product of putrefaction of gluten in

presence of water. It has since been found to exist widely distributed in animal nature; it has been obtained from the normal spleen, pancreas, salivary, lymphatic, thymus, and thyroid glands, lungs, and liver. Pathologically, its quantity in the liver is much increased in diseases of that organ, and in typhus and variola; in the bile in typhus, in the blood in leucocythæmia, and in yellow atrophy of the liver; in the urine in yellow atrophy of the liver, in typhus, and in variola; in choleraic discharges from the intestine, in pus, in the fluids of dropsy, and of atheromatous cysts. In these situations it is usually accompanied by tyrosine (*q. v.*). It is much more abundant in the tissues of the lower forms of animal life, and has also been found in vegetable tissues.

It is formed by the decomposition of nitrogenized animal and vegetable substances by heating with strong alkalies or dilute acids; by the decomposition of elastic tissues it is formed with a small quantity of tyrosine; by that of gelatinoid materials, leucine and glycine are obtained; by that of albuminoids, leucine and a small, but variable, quantity of tyrosine are formed; and that of epidermic tissues yields leucine and tyrosine. It is also one of the products of the putrefaction of animal and vegetable albuminoids, and of the action of pancreatic juice upon fibrin. It has also been formed synthetically by the action of ammonia upon bromocaproic acid in the same way that alanine is formed from bromopropionic acid (see above).

It may be obtained by a variety of methods, the most advantageous of which consists in boiling one part of horn-shavings with four parts of sulphuric acid and twelve parts of water, for thirty-six hours, renewing the water as it evaporates; the acid liquid is saturated with milk of lime and boiled again for twenty-four hours; it is then filtered through linen, a slight excess of sulphuric acid is added, and the liquid again filtered and evaporated; tyrosine first crystallizes out and is separated, after which leucine separates in crystals, which are purified by recrystallization from a small quantity of water, the crystals first formed being rejected as being contaminated with tyrosine. The leucine so obtained is further purified by solution in hot water, digestion with lead hydrate; filtration, treatment with hydrogen sulphide; filtration, treatment with animal charcoal; filtration and crystallization.

Leucine crystallizes from alcohol in soft, pearly plates, lighter than water, and somewhat resembling cholesterin; sometimes in round masses composed of closely grouped needles radiating from a centre. It is sparingly soluble in cold water; readily in warm water; almost insoluble in cold alcohol and ether; soluble in boiling alcohol, which deposits it on cooling; it is odorless and tasteless, and its solutions are neutral. Its solubility in water is increased by the presence of acetic acid or of potassium acetate. It sublimes at 170° without decomposition; if suddenly heated above 180°, it is decomposed into amylamine and carbon dioxide.

When heated to 140° with hydriodic acid under pressure, it is decomposed into caproic acid and ammonia. Nitrous acid converts it into *leucic acid*, $C_6H_{12}O_3$, water, and nitrogen. It unites with acids to form soluble crystalline salts. It also dissolves readily in solutions of alkaline hydrates, forming crystalline compounds with the metallic elements.

The formation of leucine in the body is one of the steps of the transformation of at least some part of the albuminoids into urea. That leucine is formed at the expense of the albuminoids by some fermentation-like process, there can be no doubt; as it is only discharged in the urine in certain exceptional pathological conditions, and as at the same time the

elimination of urea is greatly diminished, it seems highly probable that under normal conditions the nitrogen of leucine finally makes its exit from the body as urea, notwithstanding the fact that chemists have hitherto been unable to obtain urea from leucine artificially. As to the nature of the changes by which leucine is converted into urea in the body, we are as yet in the dark.

When leucine and tyrosine appear in the urine, that fluid is poor in urea and usually contains biliary coloring matters; the substitution of leucine for urea may be so extensive that the urine contains no urea, and contains leucine in such quantity that it crystallizes out spontaneously.

The presence of smaller quantities of leucine and tyrosine in the urine may be detected as follows: the freshly collected urine is treated with basic lead acetate, filtered, the filtrate treated with hydrogen sulphide, filtered from the precipitated lead sulphide, and the filtrate evaporated over the water-bath; leucine and tyrosine crystallize; they may be separated by extraction of the residue with hot alcohol, which dissolves the leucine and leaves the tyrosine. The leucine left by evaporation of the alcoholic solution may be recognized by its crystalline form and by the following characters: 1st, a small portion is moistened on platinum foil with nitric acid, which is then cautiously evaporated; a colorless residue remains, which, when warmed with caustic soda solution, turns yellow or brown, and by further concentration is converted into oily drops, which do not adhere to the platinum (Scherer's test); 2d, a portion of the residue is heated in a dry test-tube; it melts into oily drops, and the odor of amylamine (odor of ammonia combined with that of fusel oil) is observed; 3d, if a boiling mixture of leucine and solution of neutral lead acetate be carefully neutralized with ammonia, brilliant crystals of a compound of leucine and lead oxide separate; 4th, leucine carefully heated in a glass tube open at both ends, to 170°, sublimes without fusing, and condenses in flocculent shreds, resembling those of sublimed zinc oxide. If heated beyond 180°, the decomposition mentioned in 2d occurs.

Tyrosine, $C_9H_{11}NO_3$.

A substance which certainly does not belong to this series, and is probably an amido-acid of the aromatic series; nevertheless, as its constitution is still undetermined, and as it is almost universally found to accompany leucine in animal tissues and in the products of their decomposition, it may be considered in this place.

The methods of its formation and preparation are given under leucine.

It crystallizes from its watery and ammoniacal solutions in silky needles, arranged in stellate bundles; very sparingly soluble in cold water; almost insoluble in alcohol; more soluble in hot water. When heated it turns brown and yields an oily matter having the odor of phenol; when heated in small quantities to 270°, it is decomposed into carbon dioxide and a white solid, having the composition $C_8H_{11}NO$, which sublimes. It combines with both acids and bases.

It has been found in animal nature in the same situations as leucine. When taken into the stomach it is not altered in the economy, but is eliminated in the urine and fæces.

Tyrosine may be recognized by the following characters: 1st, its crystalline form; 2d, when heated it does not sublime, but gives off an odor

resembling that of phenol; 3d, when moistened on platinum foil with nitric acid and this carefully evaporated, it dissolves and leaves a deep yellow residue, which, when moistened with sodic hydrate solution, turns deep yellowish red and leaves, on evaporation of the soda, a dark brown residue (Scherer); 4th, when moistened on a porcelain dish with concentrated sulphuric acid and slightly warmed, it dissolves with a transient red color; the solution, diluted with water, neutralized with calcium carbonate and filtered, gives a liquid to which a *neutral* solution of ferric chloride communicates a fine violet color (Piria); 5th, if boiled with a solution of acid nitrate of mercury, a pink color is first observed, and later a red precipitate (Hoffmann, L. Meyer).

Creatine, $C_4H_9N_3O_2+Aq.$

Another complex amido-acid, which occurs as a normal constituent of the juices of muscular tissue, voluntary and involuntary, of brain, blood, and amniotic fluid. Its existence in the urine is very doubtful.

It is best obtained from the flesh of the fowl, which contains 0.32 per cent., or from beef-heart, which contains 0.14 per cent., by hashing, warming with alcohol and expressing strongly; the alcohol is distilled off, the residual liquid precipitated with lead acetate, filtered, treated with hydrogen sulphide, again filtered, the filtrate evaporated to a syrup, from which the creatine crystallizes.

It is soluble in boiling water and in alcohol, insoluble in ether; crystallizes in brilliant, oblique, rhombic prisms; neutral, tasteless, loses aq. at 100°; fuses and decomposes at higher temperatures.

When long heated with water or treated with concentrated acids, it loses H_2O, and is converted into creatinine. Baryta water decomposes it into sarcosine and urea. It is not precipitated by silver nitrate, except when it is in excess and in presence of a small quantity of potassium hydrate; the white precipitate so obtained is soluble in excess of potash, from which a jelly separates which turns black, slowly at ordinary temperatures, rapidly at 100°. A white precipitate, which turns black when heated, is also formed when a solution of creatine is similarly treated with mercuric chloride and potash.

Creatin is undoubtedly an intermediate product of disassimilation of the albuminoid constituents of the tissues in which it occurs; it is not discharged as such, but only after decomposition into creatinine and into urea, both of which increase in quantity in the urine when creatine is taken.

Creatinine, $C_4H_7N_3O$.

A product of the dehydration of creatine, is a normal and constant constituent of the urine and amniotic fluid, and has also been found to exist in the blood and muscular tissue.

It crystallizes in oblique, rhombic prisms, soluble in water and in hot alcohol; insoluble in ether. It is a strong base, has an alkaline taste and reaction, expels ammonia from the ammoniacal salts, and forms well-defined salts, among which is the double chloride of zinc and creatinine $(C_4H_7N_3O)_2ZnCl_2$, obtained in very sparingly soluble, oblique prismatic crystals, when alcoholic solutions of creatinine and zinc chloride are mixed.

The quantity of creatinine eliminated is slightly greater than that of uric acid, 0.6—1.3 gram in twenty-four hours; it is not increased by muscular exercise, but is diminished in progressive muscular atrophy. It is obtained from the urine by precipitation with zinc chloride.

COMPOUNDS OF THE ALCOHOLIC RADICALS WITH OTHER ELEMENTS.

The organic substances hitherto considered are composed of seven elements only: carbon, hydrogen, oxygen, nitrogen, chlorine, bromine, and iodine; but compounds of carbon containing every known element have been observed to exist in nature, or have been produced artificially. Of these quite a number may be considered as containing the radicals of the series C_nH_{2n+1}, which exist in the monoatomic alcohols. These bodies are almost exclusively the products of the laboratory, and resemble in constitution some of the compounds already considered.

Sulphides.—The compounds of the alcoholic radicals with sulphur are the same in constitution as those with oxygen, sulphur taking the place of oxygen:

$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O''$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O''$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S''$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S''$
Ethyl hydrate (alcohol).	Ethyl oxide (ether).	Ethyl sulphydrate (mercoptan).	Ethyl sulphide.

Similar compounds have been obtained in which the oxygen is replaced by tellurium or by selenium.

Ethyl sulphydrate, usually known as *mercaptan*, from its tendency to unite with mercury (*corpus mercurium captans*), is formed in a great variety of reactions. It is best prepared by treating alcohol with sulphuric acid, as in the preparation of sulphovinic acid (*q. v.*), mixing the crude product with excess of potash, separating from the crystals of potassium sulphate, saturating with hydrogen sulphide, and distilling.

It is a mobile, colorless liquid; sp. gr. 0.8325, at 21°; has an intensely disagreeable odor, combined of those of garlic and sulphuretted hydrogen; boils at 36.2°; ignites readily and burns with a blue flame; may be readily frozen by the cold produced by its own evaporation; neutral in reaction; sparingly soluble in water, soluble in all proportions in alcohol and ether; dissolves iodine, sulphur, phosphorus.

Potassium and sodium act with mercaptan as with alcohol, replacing the extra-radical hydrogen. In its behavior toward the oxides it more closely resembles the acids than the alcohols, being capable even of entering into double decomposition to form salts, called *sulphethylates* or *mercaptides*. Its action with mercuric oxide is characteristic, forming a white, crystalline sulphide of ethyl and mercury:

$$2\left(\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S\right) + Hg'' = \left.\begin{matrix}(C_2H_5)_2\\Hg''\end{matrix}\right\}S_2 + H_2O$$

Ethyl sulphydrate. Mercuric oxide. Ethyl-mercurial sulphide. Water.

It forms similar compounds with gold and platinum.

Ethyl sulphide, a colorless liquid; having a penetrating, disagreeable odor of garlic; boiling at 73°; insoluble in water, soluble in alcohol; in-

flammable; obtained by the action of ethyl chloride upon potassium sulphide.

Phosphines, arsines, and **stibines** are compounds resembling the amines in constitution, in which the nitrogen is replaced by phosphorus, arsenic, or antimony; like the amines, they may be primary, secondary, or tertiary:

$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}P$	$\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}As$	$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}Sb.$
Ethylamine (primary).	Ethylphospine (primary).	Diethyl-arsine (secondary).	Triethyl-stibine (tertiary).

There also exist compounds containing phosphorus, antimony, or arsenic, which are similar in constitution to the hydrates and salts of ammonium, and of the compound ammoniums:

NH_4I	$N(CH_3)_4I$	$As(CH_3)_4I$
Ammonium iodide.	Tetramethyl ammonium iodide.	Tetramethyl arsenium iodide.

Most of these compounds, which are very numerous, are as yet only of theoretic interest. One of them, however, is deserving of notice here:

Dimethyl arsine, $\left.\begin{matrix}CH_3\\CH_3\\H\end{matrix}\right\}As$—which may be considered as being the hydride of the radical $[As(CH_3)_2]$, does not exist as such; there was, however, discovered by Cadet, in 1760, a liquid known as the *fuming liquor of Cadet,* or *alkarsin,* which he obtained by distilling a mixture of potassium acetate and arsenic trioxide. This liquid was made the subject of most successful study by Bunsen, who found that it contained the oxide of the above radical, and a substance which ignited on contact with air, and which consists of the same radical united to itself $2[As(CH_3)_2]$. He subsequently found that this radical, to which he gave the name of *cacodyle* (κακός = evil), was capable of entering into a great number of other combinations. Cacodyle and its compounds are all exceedingly poisonous, especially the cyanide, an ethereal liquid, very volatile, the presence of whose vapor in inspired air, even in minute traces, produces symptoms referable both to arsenic and to hydrocyanic acid.

Organo-metallic substances are compounds of the alcoholic radicals with that class of elements usually designated as metallic. They are very numerous, usually obtained by the action of the iodide of the alcoholic radical upon the metallic element, in an atmosphere of hydrogen. They are substances which, although they have been put to no uses in the arts or in medicine, have been of great practical service in chemical research. As typical of this class of substances we may mention:

Zinc-ethyl, $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Zn$—a substance discovered in 1849, by Frankland. It is obtained by heating at 130° in a sealed tube a mixture of perfectly dry zinc amalgam with ethyl iodide; the contents of the tube are then distilled in an atmosphere of coal-gas, or hydrogen, and the distillate collected in a receiver, in which it can be sealed by fusion of the glass without contact with air.

It is a colorless, transparent, highly refracting liquid; sp. gr. 1.182; boils at 118°. On contact with air it ignites and burns with a luminous flame, bordered with green, and gives off dense clouds of zinc oxide, a property which renders it very dangerous to handle. With carbon dioxide it combines to form zinc propionate:

$$\underset{\text{Zinc ethyl.}}{Zn(C_2H_5)_2} + \underset{\text{Carbon dioxide.}}{2CO_2} = \underset{\text{Zinc propionate.}}{(C_3H_5O_2)_2Zn.}$$

On contact with water it is immediately decomposed into zinc hydrate and ethyl hydride. It is chiefly useful as an agent by which the radical ethyl can be introduced into organic molecules; thus, by the action of zinc ethyl upon acetyl chloride, a compound of acetyl and ethyl is obtained:

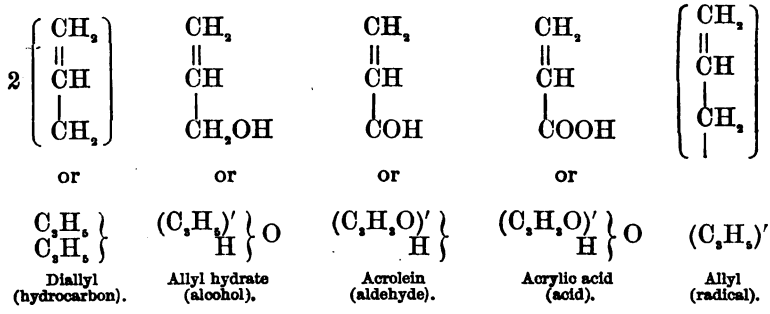
$$\underset{\text{Zinc-ethyl.}}{Zn(C_2H_5)_2} + \underset{\text{Acetyl chloride.}}{2C_2H_3OCl} = \underset{\text{Zinc chloride.}}{ZnCl_2} + \underset{\text{Acetyl-ethyl.}}{2(C_2H_3O,C_2H_5)}$$

ALLYLIC SERIES.

The compounds which we have heretofore considered may be derived more or less directly from the saturated hydrocarbons; in the derivatives, as in the hydrocarbons, the valences of the carbon atoms are all satisfied, and that in the simplest and most complete manner, two neighboring atoms of carbon always exchanging a *single* valence. There exist, however, other compounds, containing less hydrogen in proportion to carbon than those already considered, and yet resembling them in being monoatomic. These compounds have usually been considered as *non-saturated*, because all the *possible* valences are not satisfied, and the substances are therefore capable of forming products of *addition*, while the *saturated* compounds can only form products of *substitution*.

In this sense the substances composing this series are non-saturated, but they are not so in the sense that they contain carbon or other atoms whose valences are not satisfied. The following formulæ indicate the constitution of the substances of this series, and their relation to those of the previous one. It will be observed that in the allyl compounds two neighboring atoms of carbon exchange *two* valences:

CH_3	CH_3	CH_3	CH_3	CH_3
CH_2	CH_2	CH_2	CH_2	CH_2
CH_2H	CH_2OH	COH	$COOH$	CH_2
or	or	or	or	
$(C_3H_7)'H$	$(C_3H_7)'H\}O$	$(C_3H_5O)'H$	$(C_3H_5O)'H\}O$	$(C_3H_7)'$
Propyl hydride (hydrocarbon).	Propyl hydrate (alcohol).	Propionyl hydride (aldehyde).	Propionyl hydrate (acid).	Propyl (radical).



Diallyl, $\left.\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\right\}$—formerly known as *allyl,* is obtained by the action of sodium upon allyl iodide, and is not, as its empirical formula would seem to indicate, a superior homologue of acetylene and allylene (*q. v.*).

It is a colorless liquid, having a peculiar odor, somewhat resembling that of horseradish; boils at 59°; sp. gr. 0.684 at 14°; burns with a luminous flame.

Allyl iodide, C_3H_5I—is a colorless liquid, having an ethereal, alliaceous odor; boiling at 101°; sp. gr. 1.789 at 16°; obtained by the action of phosphorus triiodide upon either allylic alcohol or glycerin.

Allyl hydrate—*Allylic alcohol*—$\left.\begin{matrix}C_3H_5\\H\end{matrix}\right\}$O—may be obtained by a variety of methods:

First.—By the action of silver oxalate upon allyl iodide, allyl oxalate is formed; this is then decomposed with ammonia, and oxamide and allyl hydrate are obtained.

Second.—By the action of sodium upon dichlorhydrine in ethereal solution.

Third.—The best process consists in heating four parts of glycerin with one part of crystallized oxalic acid. In the first stage of the operation carbon dioxide is given off abundantly; as the temperature rises the formation of carbon dioxide diminishes, and again increases at about 190°, when allyl alcohol begins to be formed; at this time the receiver connected with the retort, in which the mixture is heated, is changed, and the heat increased to about 260°. The product, which is a mixture of allyl alcohol with allyl formiate, formic acid, acrolein, and glycerin, is purified by agitation with sodium carbonate and with caustic potassa, after which it is rectified, and finally distilled from quicklime.

Allylic alcohol is a colorless, mobile liquid; solidifies at −54°; boils at 97°; sp. gr. 0.8507 at 25°; soluble in water; has an odor resembling the combined odors of alcohol and essence of mustard; burns with a luminous flame.

Allyl alcohol is isomeric with propylic aldehyde and with acetone. Being an unsaturated compound, it is capable of forming products of addition with chlorine, bromine, and iodine, etc., which are isomeric or identical with products of substitution obtained by the action of the same elements upon glycerin (see Glycerides, p. 277). Oxidizing agents convert it first into acrolein, acrylic aldehyde, C_3H_4O, and finally into acrylic acid. It does not combine readily with hydrogen, but in the presence of nascent hydrogen combination takes place slowly, with formation of propylic alcohol.

Allyl oxide—*Allylic ether*—$\left.\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\right\}O$—exists in small quantities in crude essence of garlic. It is obtained as a colorless liquid, having an alliaceous odor; insoluble in water; boiling at 82°, by a number of reactions, but best by the action of allyl iodide upon sodium allyl oxide:

$$\underset{\text{Allyl iodide.}}{\left.\begin{matrix}C_3H_5\\I\end{matrix}\right\}} + \underset{\text{Sodium allyl oxide.}}{\left.\begin{matrix}C_3H_7\\Na\end{matrix}\right\}O} = \underset{\text{Sodium iodide.}}{\left.\begin{matrix}Na\\I\end{matrix}\right\}} + \underset{\text{Allyl oxide.}}{\left.\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\right\}O}$$

Allyl sulphide—*Essence of garlic*—$\left.\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\right\}S$—is obtained by the action of an alcoholic solution of potassium sulphide upon allyl iodide; also as a constituent of the volatile oil of garlic, by macerating garlic, or other related vegetables, in water and distilling. Crude essence of garlic is thus obtained as a heavy, fetid, brown oil; this is purified by redistillation below 140°; contact with potassium and subsequent redistillation form calcium chloride.

As thus obtained it is a colorless, transparent oil; lighter than water, sparingly soluble in water, very soluble in alcohol and ether; boils at 140°; has an intense odor of garlic.

This substance does not exist naturally in the plant, or at least not in quantities at all approximating to those in which it is obtained from it; it is formed during the process of extraction by the action of water, probably in a manner similar to that in which essence of mustard is formed under similar circumstances. It is to the formation of allyl sulphide, which is highly volatile, that garlic owes the odor which it emits, especially when heated with water, as in cooking.

Allyl sulphocyanate—*Essential oil of mustard*—$\left.\begin{matrix}CN\\C_3H_5\end{matrix}\right\}S$.—If the seeds of white or black mustard be strongly expressed, a bland, neutral oil is obtained, which resembles rapeseed and colza oils in its physical properties, and in being composed of the glycerides of stearic, oleic and erucic acids. The cake remaining after the expression of this oil from *black mustard*, or the black-mustard seeds themselves, pulverized and moistened with water, gives off a strong, pungent odor. If the water be now distilled, a volatile oil passes over with it, which is the crude essential oil of mustard.

In practice the powdered cake of black-mustard seeds, from which the fixed oil has been expressed, is digested with four to six parts of water for twenty-four hours, after which the water is distilled as long as any oily matter passes over; the oil is collected, dried by contact with calcium chloride, and redistilled. Essence of mustard may also be obtained synthetically by the action of allyl bromide or iodide upon potassium sulphocyanate, or by the action of allyl iodide upon silver sulphocyanate.

This essence does not exist preformed in the mustard, but results from the decomposition of a peculiar constituent of the seeds, *potassium myronate*, determined by a fermentation set up by another constituent, *myrosine*, in the presence of water—the decomposition probably occurring according to the equation—

$$\underset{\text{Potassium myronate.}}{C_{10}H_{18}NS_2O_{10}K} = \underset{\text{Allyl sulphocyanate.}}{CNS_2C_3H_5} + \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Hydropotassic sulphate.}}{SO_4HK}$$

Potassium myronate exists only in appreciable quantity in the black variety of mustard, from which it may be obtained in the shape of short, prismatic crystals, transparent, odorless, bitter; very soluble in water, sparingly so in alcohol.

Myrosine is a nitrogenized ferment existing in the white as well as in the black mustard, and in other seeds. It may be obtained from white-mustard seeds, in an impure form, by extraction with cold water, filtering and evaporating the solution at a temperature below 40°; the syrupy fluid so obtained is precipitated with alcohol, the precipitate washed with alcohol, redissolved in water, and the solution evaporated below 40° to dryness.

At temperatures above 40° myrosine becomes coagulated and incapable of decomposing potassium myronate, a change which is also produced by contact with acetic acid. As the rubefacient and vesicant actions of mustard, when moistened with water, are due to the production of allyl sulphocyanate, it is obvious that neither vinegar, acetic acid, or heat greater than 40°, should be used in the preparation of mustard cataplasms. The prepared mustard plasters or papers which are now in use are made by spreading the flour of mustard, mixed with benzol or carbon disulphide and caoutchouc, upon paper.

Pure allyl sulphocyanate is a transparent, colorless oil; sp. gr. 1.015 at 20°; boils at 143°; has a penetrating, pungent odor, sparingly soluble in water, very soluble in alcohol and ether. When exposed to the light it gradually turns brownish yellow and deposits a resinoid material. When applied to the skin it produces rubefaction, quickly followed by vesication.

Menthyl hydrate—*Menthol—Menthic alcohol—Peppermint camphor*—$\left.\begin{matrix}C_{10}H_{19}\\H\end{matrix}\right\}O$—is a superior homologue of allyl alcohol, and is a solid deposited by the essential oil of peppermint. When purified it forms colorless, prismatic crystals; insoluble in water, soluble in alcohol, ether, and in acids; fuses at 34°—36°; boils at 213°; has the odor and taste of peppermint strongly developed. It is capable of yielding, under suitable conditions, ethers of a radical, *menthyl*, and a hydrocarbon—*menthene*, $C_{10}H_{18}$.

ACIDS AND ALDEHYDES OF THE ACRYLIC SERIES.

These substances bear the same relation to the alcohols of the allyl series that the volatile fatty acids and the corresponding aldehydes bear to the ethylic series of alcohols. The following terms of the series have been obtained:

Acids. $C_nH_{n-2}O_2$.		*Aldehydes.* $C_nH_{2n-2}O$.	
Acrylic acid	$C_3O_2H_4$	Acrolein	C_3OH_4
Crotonic	$C_4O_2H_6$	Crotonic aldehyde	C_4OH_6
Angelic	$C_5O_2H_8$		
Pyroterebic	$C_6O_2H_{10}$		
Oleic	$C_{18}O_2H_{34}$		

The acids of this series differ from those containing the same number of carbon atoms in the formic series, by containing two atoms of hydro-

gen less; they are readily converted into acids of the formic series by the action of potassium in fusion, which forms with them the potassium salt of acetic acid and that of the acid of the formic series containing the complementary number of carbon atoms, thus:

$$\underset{\text{Acrylic acid.}}{C_3H_4O_2} + 2KHO = \underset{\text{Acetate.}}{C_2H_3O_2K} + \underset{\text{Formiate.}}{CHO_2K} + H_2$$

Acrylic acid—$C_3H_3O\}O$—is obtained by oxidation of acrolein, acrylic aldehyde, by silver oxide, and is formed in a number of other reactions; as a product of the oxidation of acrolein, it is formed when grease is strongly heated.

It is a colorless, highly acid liquid; has a penetrating odor; solidifies at 7°; boils at 140°; distils unchanged with vapor of water.

Nascent hydrogen unites with it to form proprionic acid. It readily forms crystallized salts and ethers. There exist products of substitution with chlorine and bromine.

Acrylic aldehyde—*Allylic aldehyde*—*Acrolein*—$C_3H_3O\}$—When the fats and fixed oils are decomposed by heat, a disagreeable, irritating odor is produced, which is due to the formation of acrolein by the dehydration of the glycerin contained in the fatty material. Acrolein may be obtained by heating glycerin with strong sulphuric acid, or with hydropotassic sulphate. Glycerin is the alcohol (hydrate) of a radical having the same composition as allyl, but so differing from it in constitution as to be trivalent in place of univalent.

$$\underset{\text{Glycerin.}}{(C_3H_5)'''(OH)_3} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Acrolein.}}{(C_3H_3O)'H}$$

The condensed product of this reaction, which must be conducted in an atmosphere of carbon dioxide, in a capacious retort and receiver, and in such a way that the uncondensed products are discharged into the open air, are purified by contact with lead oxide, and subsequent distillation from calcium chloride.

Acrolein is a colorless, limpid liquid; lighter than water; boils at 52.4°; sparingly soluble in water; more soluble in alcohol; very volatile, its vapor having a very pungent odor and producing irritation and suffocation to such a degree that the presence of a very small quantity in a confined space renders the atmosphere irrespirable; its taste is caustic. When freshly prepared it is neutral in reaction, but on contact with air it rapidly becomes acid by oxidation. For the same reason it does not keep well, even in closed vessels; on standing it deposits a flocculent material, which has been called *disocryl*, while at the same time formic, acetic, and acrylic acids are formed.

Oxidizing agents convert acrolein into acrylic acid, or, if they be energetic, into a mixture of formic and acetic acids. The caustic alkalies produce from it resinoid substances similar to those formed from acetic aldehyde. With ammonia it forms a crystalline, odorless compound, which behaves as a base.

Acrolein is formed whenever glycerin, or any substance containing it or its compounds with the fatty acids, is heated to a temperature sufficient

to effect its decomposition; for this reason, and because of the irritating action of the acrolein, the heavy petroleum-oils are preferable to those of vegetable or animal origin for the lubricating of machinery operated in enclosed places.

Crotonic acid, $\left.\begin{matrix}C_4H_5O\\H\end{matrix}\right\}O$—was first obtained from croton-oil, *oleum tiglii* (U. S.), in which it exists in combination with glycerin, and accompanied by the glycerin ethers of several other fatty acids; it is, however, neither the vesicant nor the purgative principle of the oil. It may be obtained by saponification of croton-oil, or, better, by the action of potassium hydrate upon allyl cyanide:

$$\underset{\text{Allyl cyanide.}}{C_3H_5CN} + \underset{\text{Potassium hydrate.}}{KHO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Potassium crotonate.}}{C_4H_5O,OK} + \underset{\text{Ammonia.}}{NH_3}$$

It is an oily liquid; solidifies at −5°; acrid in taste; gives off highly irritating vapors at temperatures slightly above 0°. When taken internally it acts as an irritant poison.

An acid obtained by oxidation of crotonic aldehyde is probably an isomere, as it is in the form of crystals at ordinary temperatures, and only fuses at 73°.

Crotonic acid forms well-defined salts, and products of substitution with chlorine and bromine.

Crotonic aldehyde, $\left.\begin{matrix}C_4H_5O\\H\end{matrix}\right\}$.—If aldehyde, water, and hydrochloric acid be mixed together at a low temperature, and the mixture exposed to diffused daylight for some days, an oily liquid is formed, which, after purification, has the composition $C_4H_8O_2$. This substance, known as *aldol*, when exposed to heat, is decomposed into water and crotonic aldehyde:

$$\underset{\text{Aldol.}}{C_4H_8O_2} = \underset{\text{Water.}}{H_2O} + \underset{\text{Crotonic aldehyde.}}{C_4H_6O}$$

Crotonic aldehyde is a colorless liquid; boils at 105°; gives off highly irritating vapors. It is only of interest as bearing the same relation to croton chloral that aldehyde does to chloral.

Croton chloral—*Trichlorocroton aldehyde*—$\left.\begin{matrix}C_4H_2Cl_3O\\H\end{matrix}\right\}$—a substance which has been recently introduced into medicine as an anæsthetic whose action is particularly directed to the sensory nerves distributed to the head and face. It is prepared by directing a current of chlorine through acetic aldehyde as ordinary chloral is obtained by the action of chlorine upon ethylic alcohol (see p. 201). The first action of the chlorine is to convert ethylic aldehyde into crotonic aldehyde by condensation and elimination of water; in the second stage of the reaction the substitution of three atoms of chlorine for an equal number of atoms of hydrogen in the croton aldehyde thus formed takes place.

Angelic acid, $\left.\begin{matrix}C_5H_7O\\H\end{matrix}\right\}O$—exists in angelica root, *Angelica* (U. S.), in the flowers of chamomile, *Anthemis* (U. S.), and in croton-oil.

It crystallizes in colorless prisms, which fuse at 45.5°; boils at 185°;

has an aromatic odor and an acid, pungent taste; sparingly soluble in cold water; readily soluble in hot water, alcohol, and ether. By the action of heat it is converted into its isomere, *methylcrotonic acid*, $\left.\begin{matrix}C_4H_4(CH_3)O\\H\end{matrix}\right\}O$.

The *Essence of chamomile, Oleum anthimidis* (Br.), is a mixture in varying proportions of compound ethers, in which amyl and butyl angelates predominate.

Oleic acid, $\left.\begin{matrix}C_{18}H_{33}O\\H\end{matrix}\right\}O$—exists as its glycerin ether, *olein*, in most, if not in all, the fats and in all fixed oils. It is obtained in an impure form on a large scale, industrially, as a by-product in the manufacture of candles. This product is, however, very impure; to purify it, it is first cooled to zero, the liquid portion collected, cooled to −10°, expressed, and the solid portion collected; this is melted and treated with half its weight of massicot; the lead oleate so obtained is dissolved out by ether; the decanted ethereal solution is shaken with hydrochloric acid, the ethereal layer decanted and evaporated, when it leaves oleic acid, contaminated with a small quantity of oxyoleic acid, from which it can be purified only by a tedious process.

Pure oleic acid is a white, pearly, crystalline solid, which fuses to a colorless liquid at 14°; when cold liquid oleic acid is warmed, it solidifies at 4°; it is odorless and tasteless; soluble in alcohol, ether, and cold sulphuric acid; insoluble in water; sp. gr. 0.808 at 19°; neutral in reaction. It can be distilled in vacuo without decomposition, but when heated in contact with air it is decomposed with formation of hydrocarbons, volatile fatty acids, and sebacic acid. It dissolves the fatty acids readily, forming mixtures whose consistency varies with the proportions of liquid and solid acid which they contain. The solid acid is but little altered by exposure to air, but when liquid it absorbs oxygen rapidly, becomes yellow, rancid, acid in reaction, and incapable of solidifying when cooled; these changes take place the more rapidly the higher the temperature.

Chlorine and bromine attack oleic acid with formation of products of substitution. If oleic acid be heated with an excess of caustic potassa to 200°, it is decomposed into palmitic and acetic acids:

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + 2KHO = \underset{\substack{\text{Potassium}\\\text{palmitate.}}}{C_{16}H_{31}O_2K} + \underset{\substack{\text{Potassium}\\\text{acetate.}}}{C_2H_3O_2K} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{H_2}$$

A reaction which is utilized industrially to obtain hard soaps, palmitates, form olein, which itself only forms soft soaps. Cold sulphuric acid dissolves oleic acid, and deposits it unaltered on the addition of water; but if the acid solution be heated it turns brown and gives off sulphur dioxide. Nitric acid oxidizes it energetically with formation of a number of volatile fatty acids and acids of another series—suberic, adipic, etc. The oleates of the alkaline metals are soft, soluble soaps; those of the earthy metals are insoluble in water, but soluble in alcohol and in ether.

Elaidic acid is an isomere of oleic acid, produced by the action upon it of nitrous acid in the preparation of *Unguentum hydrargyri nitratis* (U. S., Br.). The nitrous fumes formed convert the oleic acid contained in the oil and lard used into elaidic acid, which exists in the ointment in combination with mercury.

POLYATOMIC COMPOUNDS.

The organic compounds hitherto considered may be looked upon as compounds of *univalent* carbon radicals, these radicals existing in the alcohols and acids in combination with an atom each of oxygen and hydrogen; they are called *monoatomic* because they contain a single atom of hydrogen capable of being replaced by an alcoholic radical. There exist other carbon compounds, in which the radicals, containing a less number of hydrogen atoms as compared with the number of carbon atoms, have a valence greater than one; these radicals form acids, alcohols, etc., in which the number of atoms of replaceable hydrogen is greater than one, and which are designated as polyatomic.

NON-SATURATED HYDROCARBONS.

Besides the compounds of carbon and hydrogen described on pp. 149–157, in which all the valences of the carbon atoms are satisfied either by the attachment of hydrogen atoms, or by the interchange of a *single* valence between neighboring carbon atoms, there exist many others in which the proportion of hydrogen to carbon is less. These compounds are *non-saturated* in this, that they are capable of uniting directly with atoms of other elements, or with radicals, to form products of addition, while the composition of the *saturated* hydrocarbons can only be modified by *substitution;* they are not, however, to be considered as containing any unsatisfied valence.

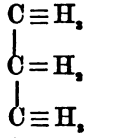
These hydrocarbons are very numerous, and may be arranged in homologous series, as shown in the following table (p. 228), each succeeding series containing a less amount of hydrogen in proportion to the carbon:

Each series and its derivatives will be considered in the order given in the table.

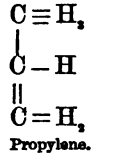
SECOND SERIES OF HYDROCARBONS—OLEFINES.

Series C_nH_{2n}.

The terms of this series contain two atoms of hydrogen less than the corresponding terms of the first series; they differ in constitution in this, that, while in the first series a single valence is exchanged between each two neighboring carbon atoms, in the second series two valences are exchanged between two of the carbon atoms:



Propane.



Propylene.

They are designated as *olefines*, a name derived from a property of the second in the series, which was formerly known as olefiant gas; or, to dis-

HYDROCARBONS.

1st Series. C_nH_{2n+2}	2d Series. C_nH_{2n}	3d Series. C_nH_{2n-2}	4th Series. C_nH_{2n-4}	5th Series. C_nH_{2n-6}	6th Series. C_nH_{2n-8}	7th Series. C_nH_{2n-10}	8th Series. C_nH_{2n-12}	9th Series. C_nH_{2n-14}	10th Series C_nH_{2n-16}	11th Series C_nH_{2n-18}	12th Series C_nH_{2n-20}
CH_4 Methane.	CH_2 Methene.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
C_2H_6 Ethane.	C_2H_4 Ethene.	C_2H_2 Acetylene.	.....	.....	.....	.....	.....	.....	.....	.....	.....
C_3H_8 Propane.	C_3H_6 Propene.	C_3H_4 Allylene.	C_3H_2	.....	.....	.....	.....	.....	.....	.....	.....
C_4H_{10} Butane.	C_4H_8 Butene.	C_4H_6 Crotonylene.	C_4H_4	C_4H_2	.....	.....	.....	.....	.....	.....	.....
C_5H_{12} Pentane.	C_5H_{10} Pentene.	C_5H_8 Valerylene.	C_5H_6 Valylene.	C_5H_4	C_5H_2	.....	.....	.....	.....	.....	.....
C_6H_{14} Hexane.	C_6H_{12} Hexene.	C_6H_{10} Hexylene.	C_6H_8	C_6H_6 Benzene.	C_6H_4	C_6H_2	.....	.....	.....	.....	.....
C_7H_{16} Heptane.	C_7H_{14} Heptene.	C_7H_{12} Œnanthylidene	C_7H_{10}	C_7H_8 Toluene.	C_7H_6	C_7H_4	C_7H_2	.....	.....	.....	.....
C_8H_{18} Octane.	C_8H_{16} Octene.	C_8H_{14} Caprylidene.	C_8H_{12}	C_8H_{10} Xylene.	C_8H_8 Cinnamene.	C_8H_6	C_8H_4	C_8H_2	.....	.....	.....
C_9H_{20} Nonane.	C_9H_{18} Nonene.	C_9H_{16}	C_9H_{14}	C_9H_{12} Cumene.	C_9H_{10}	C_9H_8	C_9H_6	C_9H_4	C_9H_2	.....	.....
$C_{10}H_{22}$ Decane.	$C_{10}H_{20}$ Decene.	$C_{10}H_{18}$ Decenylene.	$C_{10}H_{16}$ Terebenthene.	$C_{10}H_{14}$ Cymene.	$C_{10}H_{12}$	$C_{10}H_{10}$ Naphthydrene	$C_{10}H_8$ Naphthalene.	$C_{10}H_6$	$C_{10}H_4$	$C_{10}H_2$	.....
$C_{11}H_{24}$ Undecane.	$C_{11}H_{22}$ Undecene.	$C_{11}H_{20}$	$C_{11}H_{18}$	$C_{11}H_{16}$ Laurene.	$C_{11}H_{14}$	$C_{11}H_{12}$	$C_{11}H_{10}$	$C_{11}H_8$	$C_{11}H_6$	$C_{11}H_4$	$C_{11}H_2$
$C_{12}H_{26}$ Dodecane.	$C_{12}H_{24}$ Dodecene.	$C_{12}H_{22}$	$C_{12}H_{20}$	$C_{12}H_{18}$	$C_{12}H_{16}$	$C_{12}H_{14}$	$C_{12}H_{12}$	$C_{12}H_{10}$ Acenaphthalene.	$C_{12}H_8$	$C_{12}H_6$	$C_{12}H_4$
$C_{13}H_{28}$ Tridecane.	$C_{13}H_{26}$ Tridecene.	$C_{13}H_{24}$	$C_{13}H_{22}$	$C_{13}H_{20}$	$C_{13}H_{18}$	$C_{13}H_{16}$	$C_{13}H_{14}$	$C_{13}H_{12}$	$C_{13}H_{10}$ Fluorene.	$C_{13}H_8$	$C_{13}H_6$
$C_{14}H_{30}$ Tetradecane.	$C_{14}H_{28}$ Tetradecene.	$C_{14}H_{26}$	$C_{14}H_{24}$	$C_{14}H_{22}$	$C_{14}H_{20}$	$C_{14}H_{18}$	$C_{14}H_{16}$	$C_{14}H_{14}$	$C_{14}H_{12}$ Stilbene.	$C_{14}H_{10}$ Anthracene.	$C_{14}H_8$

tinguish them from the terms of the first series, by the terminations *ylene* or *ene*, thus, the second is called *ethylene* or *ethene*. They behave as divalent radicals.

Methene—*Methylene*—CH_2—is of doubtful existence, known only in combination. **Ethene**—*Ethylene—Olefiant gas—Elayl—Heavy carburetted hydrogen*—$\overset{CH_2}{\underset{CH_2}{\|}}$—is formed by the dry distillation of fats, resins, wood, and coal, and is one of the most important constituents of illuminating gas. It is also obtained by the dehydration of alcohol or ether.

It has been obtained synthetically in three ways: 1st, by passing a mixture of hydrogen sulphide and carbon monoxide over iron or copper heated to redness; 2d, by heating acetylene in the presence of hydrogen, or by the action of nascent hydrogen upon copper acetylide; 3d, by the action of hydrogen upon the chloride C_2Cl_4, obtained by the action of chlorine upon carbon disulphide.

It is prepared in the laboratory by the dehydration of alcohol by sulphuric acid: a mixture of four parts by weight of sulphuric acid and one part of alcohol is placed in a flask containing enough sand to form a thin paste, and gradually heated to about 170°; the gas, which is given off in abundance, is purified by causing it to pass through wash-bottles containing water, an alkaline solution, and concentrated sulphuric acid, and may be collected over water.

Pure ethylene is a colorless gas; tasteless; has a faint odor resembling that of salt water, or an ethereal odor when impure; irrespirable; sparingly soluble in water, more soluble in alcohol. It burns with a luminous, white flame, and forms explosive mixtures with air and oxygen. When heated for some time at a dull red heat it is converted into acetylene, ethyl and methyl hydrides, a tarry product, and carbon.

Ethylene readily enters into combination. It unites with hydrogen to form ethyl hydride, C_2H_6. With oxygen it unites explosively on the approach of a flame, with formation of carbon dioxide and water. Oxidizing agents, such as potassium permanganate in alkaline solution, convert it into oxalic acid and water. A mixture of chlorine and ethene, in the proportion of two volumes of the former to one of the latter, unite with an explosion on contact with flame, the union being attended with a copious deposition of carbon and the formation of hydrochloric acid. Chlorine and ethene, mixed in equal volumes and exposed to diffused daylight, unite slowly, with formation of an oily liquid; *ethene chloride*, $C_2H_4Cl_2$; *Dutch liquid*, to whose formation ethene owes the name *olefiant gas*. By suitable means ethene may also be made to yield chlorinated products of substitution, the highest of which is *carbon tetrachloride*, C_2Cl_4. Bromine and iodine also form products of addition and of substitution with ethene. By union with $(OH)_2$ it forms glycol (*q. v.*). It slowly dissolves in ordinary sulphuric acid, with formation of sulphovinic acid; with fuming sulphuric acid it combines with elevation of temperature and formation of ethionic anhydride.

When inhaled, diluted with air, ethene produces effects somewhat similar to those of nitrous oxide.

The higher terms of this series are of theoretical interest only, except the fifth.

Pentene—*Amylene* or *valerine*—C_5H_{10}—a colorless, mobile liquid, boiling at 39°; obtained by heating amylic alcohol with a concentrated solution of zinc chloride. Its use as an anæsthetic has been suggested.

Ethene chloride—*Bichloride of ethylene—Dutch liquid*— $\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}$ is obtained by passing a current of ethene through a retort in which chlorine is being generated and connected with a cooled receiver. The distillate is washed with a solution of caustic potassa, afterward with water, and is finally rectified.

It is a colorless, oily liquid, which boils at 82.5°; has a sweetish taste and an ethereal odor. It is isomeric, but not identical with the chloride of monochlorinated ethyl, $\begin{matrix}C_2H_4Cl\\|\\Cl\end{matrix}$, which boils at 64°. It is capable of fixing other atoms of chlorine by substitution for hydrogen, and thus forming a series of chlorinated derivatives, the highest of which is C_2Cl_6.

DIATOMIC ALCOHOLS.

Series $C_nH_{2n+2}O_2$.

These substances, which are of great theoretical interest, were discovered in 1856 by Wurtz, and are usually designated as *glycols*. They are the hydrates of the hydrocarbons of the series C_nH_{2n}, and consist of those hydrocarbons, playing the part of divalent radicals, united with two groups OH; their general typical formula is then $\left.\begin{matrix}(C_nH_{2n})''\\H_2\end{matrix}\right\}O_2$. We have seen (p. 150) that the primary monoatomic alcohols contain the group of atoms $(CH_2OH)'$ united with $n(C_nH_{2n+1})$; the *primary* glycols are similarly constructed, and consist of twice the group (CH_2OH), united in the higher terms to $n(C_nH_{2n})$. The constitution of the glycols and their relations to the monoatomic alcohols is indicated by the following formulæ:

$\begin{matrix}CH_2OH\\|\\CH_2\\|\\CH_3\end{matrix}$ Primary propyl acohol.

$\begin{matrix}CH_2OH\\|\\CH_2\\|\\CH_2OH\end{matrix}$ Primary propyl glycol.

As the monoatomic alcohols are such by containing in their molecules a group (OH), closely attached to an electro-positive group, and capable of removal and replacement by an electro-negative group or atom, so the glycols are *diatomic* by the fact that they contain two such groups (OH); as the monoatomic alcohols are therefor only capable of forming a single ether with a monobasic acid, the glycols are capable of forming two such ethers:

$\begin{matrix}CH_2\,(C_2H_3O_2)'\\|\\CH_3\end{matrix}$ Ethyl acetate.

$\begin{matrix}CH_2\,(C_2H_3O_2)'\\|\\CH_2OH\end{matrix}$ Monoacetic glycol.

$\begin{matrix}CH_2\,(C_2H_3O_2)'\\|\\CH_2\,(C_2H_3O_2)'\end{matrix}$ Diacetic glycol.

For the products of oxidation of the glycols, see p. 232 *et seq.*

Ethene glycol—*Ethylene glycol* or *Alcohol* or *Hydrate*— $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$.—This, the best known of the glycols, was first obtained by Wurtz. It is prepared by the action of dry silver acetate upon ethylene bromide:

$$\underset{\text{Ethylene bromide.}}{C_2H_4Br_2} + \underset{\text{Silver acetate.}}{2C_2H_3O_2Ag} = \underset{\text{Silver bromide.}}{2AgBr} + \underset{\text{Diacetic glycol.}}{(C_2H_3O_2)_2C_2H_4}$$

The ether so obtained is purified by redistillation, and decomposed by heating for some time with barium hydrate:

$$\underset{\text{Diacetic glycol.}}{(C_2H_3O_2)_2C_2H_4} + \underset{\text{Barium hydrate.}}{BaO_2H_2} = \underset{\text{Barium acetate.}}{(C_2H_3O_2)_2Ba} + \underset{\text{Glycol.}}{C_2H_4,O_2H_2}$$

It is a colorless, slightly viscous liquid; odorless; faintly sweet; sp. gr. 1.125 at 0°; boils at 197°; sparingly soluble in ether; very soluble in water and in alcohol.

It is not oxidized by simple exposure to air, but on contact with platinum black it is oxidized to glycolic acid; more energetic oxidants transform it into oxalic acid. Chlorine acts slowly upon glycol in the cold; more rapidly under the influence of heat, producing chlorinated and other derivatives. By the action of dry hydrochloric acid upon cooled glycol, a product is formed intermediate between it and ethylene chloride, a neutral compound—*ethene chlorhydrate* or *ethene chlorhydrin*, $\begin{matrix}CH_2OH\\|\\CH_2Cl\end{matrix}$, which boils at 130°.

Ethene oxide—*Ethylene oxide*—$(C_2H_4)''O$.—This substance, isomeric with aldehyde, is obtained by the action of potassium hydrate upon ethene chlorhydrate, mentioned above.

It is a transparent, volatile liquid; boils at 13.5°; gives off inflammable vapors; mixes with water in all proportions. It is capable of uniting directly with water to form glycol; and with hydrochloric acid gas to regenerate ethene chlorhydrate.

The superior homologues of ethene glycol and of ethene oxide are only of interest from a theoretical point of view.

Taurine, $SO_3C_2H_7N$—is isomeric with a derivative of glycol, *isethionamide*. It is obtained from ox-bile by boiling with dilute hydrochloric acid; decanting and concentrating the liquid; separating from the sodium chloride which crystallizes; evaporating further, and precipitating with alcohol. The deposit is purified by recrystallization from alcohol.

It crystallizes in large, transparent, oblique, rhombic prisms, permanent in air, quite soluble in water, almost insoluble in absolute alcohol and ether.

Taurine has acid properties and forms salts; it is not attacked by sulphuric, nitric or nitromuriatic acid, but is oxidized by nitrous acid, with formation of water, nitrogen, and isethionic acid.

It exists in the animal economy, in the bile in taurocholic acid (*q. v.*); and has also been detected in the intestine and fæces, muscle, blood, liver, kidneys, and lungs; the *pneumic acid*, described as existing in the lung, is taurine. When taken internally, it is eliminated by the urine, not in its own form, but as *taurocarbamic* or *isethionuric acid*, $C_3H_8N_2SO_6$.

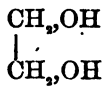
ACIDS DERIVED FROM THE GLYCOLS.

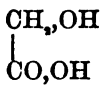
As the acids of the acetic series are obtained from the primary monoatomic alcohols by the substitution of O for H_2 in the characterizing group CH_2OH:

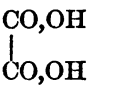

Ethyl alcohol.


Acetic acid.

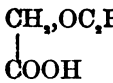
so the diatomic alcohols may, by oxidation, be made to yield acids, formed by the same substitution of O for H_2. But the glycols differ from the monoatomic alcohols in containing two groups CH_2OH, and they consequently yield two acids, as the substitution occurs in one or both of the alcoholic groups:

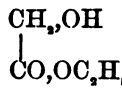

Ethene glycol.

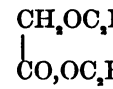

Glycolic acid.

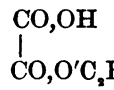

Oxalic acid.

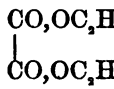
A study of these two acids shows them to be possessed of peculiar differences of function. Each of them contains two groups (OH), whose hydrogen is capable of replacement by an acid or alcoholic radical:


Ethylglycolic acid.


Ethyl glycolate.


Ethyl ethylglycolate.


Ethyloxalic acid.


Ethyl oxalate.

They are, therefor, both said to be *diatomic*. The ability, however, of the two acids to form salts is not the same, for while oxalic acid is capable of forming two salts of univalent metals, and a salt of a divalent metal with a single molecule of the acid; glycolic acid only forms a single salt of an univalent metal, and two of its molecules are required to form a salt of a divalent metal; in other words, glycolic acid is monobasic while oxalic acid is dibasic. It is only that atom of hydrogen which is contained in the electro-negative group COOH, which is replaceable as acid hydrogen, while that of the electro-positive group CH_2OH is only replaceable, as is the corresponding hydrogen of an alcohol.

In general terms, therefor, the *atomicity* of an organic acid may be greater than its *basicity*, the former representing the number of hydrogen atoms contained in its molecule, which are capable of being displaced by alcoholic radicals, while the latter represents the number of hydrogen atoms replaceable by electro-positive elements or radicals, with formation of salts or of ethers.

There may, therefor, be obtained from the glycols, by more or less complete oxidation, two series of acids; those of the first are diatomic and monobasic; those of the second diatomic and dibasic.

DIATOMIC AND MONOBASIC ACIDS.

Series $C_nH_{2n}O_2$.

The acids of this series at present known are:

(Carbonic acid).....CO_2H_2	Butylactic acid..$C_4O_3H_8$	Leucic acid.....$C_6O_3H_{12}$
Glycolic acid.....$C_2O_3H_4$	Oxyvaleric acid.$C_5O_3H_{10}$	(?)Œnanthic acid.$C_{14}O_2H_{28}$
Ethyleno-lactic acid..$C_3O_3H_6$		

The first-named of these acids, although not capable, so far as yet known, of existing in the free state, is widely represented in nature in the shape of its salts, the carbonates. Its position in this series is an anomaly, and at first sight a contradiction, as it is certainly not a monobasic, but a distinctly dibasic acid, or, more properly speaking, would be such were it obtained in a state of purity; it is, however, in this position as the inferior homologue of glycolic acid that carbonic acid is most naturally placed, and the dibasic nature of the latter acid does not present any valid objection to such a position, for if we consider one term of a series as derivable from its superior homologue by the subtraction of CH_2, and if we bear in mind that the basic nature of the hydrogen atom in a group OH depends upon its close union with the group CO (or with some other electro-negative group), it will become evident that the inferior homologue of glycolic acid must contain two groups OH united to one CO, and must, therefor, be dibasic:

$$\underset{\text{Glycolic acid.}}{\begin{matrix}CH_2OH\\|\\CO,OH\end{matrix}} - CH_2 = \underset{\text{Carbonic acid.}}{\begin{matrix}OH\\|\\CO,OH\end{matrix}} \quad \text{or} \quad CO\begin{matrix}OH\\OH\end{matrix}$$

The other acids of the series are formed: *First.*—By the partial oxidation of the corresponding glycol:

$$\underset{\text{Glycol.}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}} + O_2 = \underset{\text{Glycolic acid.}}{\begin{matrix}CH_2OH\\|\\CO,OH\end{matrix}} + \underset{\text{Water.}}{\begin{matrix}H\\H\end{matrix}}O$$

Second.—By the combined action of water and silver oxide upon the monochlor-acid of the acetic series, or by heating the alkaline salt of such an acid with water or potassium hydrate:

$$\underset{\substack{\text{Potassium}\\\text{monochloracetate.}}}{\begin{matrix}CH_2Cl\\|\\COOK\end{matrix}} + \underset{\text{Water.}}{\begin{matrix}H\\H\end{matrix}}O = \underset{\text{Glycolic acid.}}{\begin{matrix}CH_2OH\\|\\CO,OH\end{matrix}} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{KCl}$$

Third.—By reducing the corresponding acid of the oxalic series by nascent hydrogen:

$$\underset{\text{Oxalic acid.}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} + 2H_2 = \underset{\text{Glycolic acid.}}{\begin{matrix}CH_2OH\\|\\COOH\end{matrix}} + \underset{\text{Water.}}{\begin{matrix}H\\H\end{matrix}}O$$

Carbonic Acid, $CO\langle^{OH}_{OH}$.

Although this acid has not been isolated, it is probable that it exists in aqueous solutions of carbon dioxide, which have an acid reaction, while the dry oxide is neutral to test-paper. Its salts, the carbonates, are widely distributed in nature, and have the general composition $CO\langle^{OM'}_{OH}$, $CO\langle^{OM'}_{OM'}$, or $CO\langle^{O}_{O}\rangle M'$.

Oxides of Carbon.

These are two in number:

Carbon monoxide ..... CO
Carbon dioxide ..... CO_2

Carbon Monoxide.

Carbonic oxide—Carbonous oxide—CO—was discovered in 1799, by Priestley. It does not exist in nature, but is formed whenever carbon is burned with a supply of air insufficient to the formation of carbon dioxide; when carbon dioxide is partially reduced by passage over red-hot charcoal, iron, zinc, etc., and when vapor of water is decomposed by coal heated to bright redness.

When required in the laboratory, it is obtained either: 1st, by passing dry carbon dioxide over red-hot charcoal; or, 2d, by heating together oxalic and sulphuric acids:

$C_2O_4H_2$	+	SO_4H_2	=	SO_4H_2	+	H_2O	+	CO	+	CO_2
Oxalic acid.		Sulphuric acid.		Sulphuric acid.		Water.		Carbon monoxide.		Carbon dioxide.

The resulting gas is passed through wash-bottles containing lime-water, which retains the dioxide.

It is a colorless, odorless, tasteless gas; has been recently liquefied by Cailletet; sp. gr. 0.9678—A, 14 H; very sparingly soluble in water and in alcohol, its solubility in the latter fluid being remarkable for not varying between 0° and 20°.

It burns in air with formation of carbon dioxide and with a blue flame; its mixtures with air and oxygen are explosive on contact with flame if the proportion be not too far removed from CO:O; it is also oxidized to CO_2 in the cold by chromic acid. The most valuable property of carbon monoxide is its power of reducing many metallic oxides at a red heat, a property which is largely utilized in metallurgy. It is rapidly absorbed by ammoniacal solutions of the cuprous salts, a property utilized in gas-analysis; it is also absorbed by hot potassium hydrate solution, with formation of potassium formiate. Being a non-saturated compound, it readily unites directly with other elements, as with oxygen, to form CO_2

and with chlorine to form $COCl_2$, the latter a colorless, suffocating gas, known as *phosgene*, or *carbonyl chloride*.

Toxicology.—Carbon monoxide is an exceedingly poisonous gas, and is the chief toxic constituent of the gases given off from blast-furnaces, from defective flues, and open coal or charcoal fires, and of illuminating gas. An atmosphere containing but a small proportion of this gas produces asphyxia and death, even if the quantity of oxygen present be equal to or even greater than that normally existing in the atmosphere; 0.5 per cent. of carbon monoxide in air is sufficient to kill a small bird in a few moments, and one per cent. proves fatal to small mammals.

Poisoning by carbon monoxide may occur in several ways. By inhalation of the gases discharged from blast-furnaces and from copper-furnaces, the former containing twenty-five to thirty-two per cent., and the latter thirteen to nineteen per cent. of carbon monoxide. By the fumes given off from charcoal burned in a confined space—a favorite means of suicide, especially in France—the gas produced by this combustion is chiefly a mixture of the two oxides of carbon, the dioxide predominating largely, especially when the combustion is most active. The following is given by Leblanc as the composition of an atmosphere produced by burning charcoal in a confined space, and which proved rapidly fatal to a dog: oxygen, 19.19; nitrogen, 76.62; carbon dioxide, 4.61; carbon monoxide, 0.54; marsh-gas, 0.04. Obviously the deleterious effects of charcoal-fumes are more rapidly fatal in proportion as the combustion is imperfect and the room small and ill-ventilated.

A fruitful source of carbon monoxide poisoning, sometimes fatal, but more frequently producing languor, headache, and debility, is to be found in the stoves, furnaces, etc., used in heating our dwellings and other buildings, especially when the fuel is anthracite coal. This fuel produces in its combustion, when the air-supply is not abundant, considerable quantities of carbon monoxide, to which a further addition may be made by a reduction of the dioxide, also formed, in passing over red-hot iron; this poisonous gas may find its way into the rooms either through cracks or other defects in the stoves, flues, or pipes; by occasional downward currents of air passing over fires in open fireplaces, or, much more frequently, by direct passage through the heated metal. Experiment has shown that metals, notably cast-iron, are quite pervious to gases when heated to redness; when, therefor, a stove or the fire-box of a hot-air furnace becomes red-hot, a portion of the gases formed, by the combustion of the fuel passes through the pores of the metal to contaminate the air without, and give rise to carbonic oxide poisoning to a degree depending upon the degree of imperfection of the ventilation, the nature of the fuel, and the amount of air supplied to it. The obvious precautions required to avoid this form of what may be called chronic carbonic oxide poisoning, and which is by no means uncommon, are: 1st, to have the stoves or furnaces lined with fire-clay, which tends to prevent their overheating and to diminish their perviousness to gases; 2d, to avoid heating to redness; 3d, to furnish an abundant supply of air to the fuel; 4th, to secure proper ventilation; and 5th, in the case of hot-air furnaces, to obtain, by an abundant supply of external air to the air-chamber, a large supply of moderately heated air rather than a small quantity of very hot air.

Of late years cases of fatal poisoning by coal-gas are of very frequent occurrence, caused either by accidental inhalation, by inexperienced persons blowing out the gas, or by suicides. There can be little doubt that the most actively poisonous ingredient of coal-gas is carbon monoxide,

which exists in the ordinary illuminating gas in the proportion of 4 to 7.5 per cent., and in water-gas, made by decomposing superheated steam by passage over red-hot coke, and subsequent charging with vapor of hydrocarbons, in the large proportion of thirty to thirty-five per cent.

The method in which carbon monoxide produces its fatal effects is by forming with the blood-coloring matter a compound which is more stable than oxyhæmoglobin, and thus causing asphyxia by destroying the power of the blood-corpuscles of carrying oxygen from the air to the tissues. This compound of carbonic oxide and hæmoglobin is quite stable, and hence the symptoms of this form of poisoning are very persistent, lasting until the place of the coloring-matter thus rendered useless is supplied by new-formation. The prognosis is very unfavorable when the amount of the gas inhaled has been at all considerable; the treatment usually followed, *i. e.*, artificial respiration, and inhalation of oxygen, failing to restore the altered coloring-matter. There would seem to be no form of poisoning in which transfusion of blood is more directly indicated than in that by carbon monoxide.

Detection after death.—The blood of those asphyxiated by carbon monoxide is persistently bright red in color; when suitably diluted and examined with the spectroscope, it presents two absorption-bands very similar to those of oxyhæmoglobin (see p. 369), but more equal to each other in intensity and slightly nearer the violet end of the spectrum; owing, however, to the greater stability of the carbonic oxide compound, its spectrum may be readily distinguished from that of the oxygen compound by the addition of a reducing agent (an ammoniacal solution of ferrous tartrate), which changes the spectrum of oxyhæmoglobin to the single-band spectrum of reduced hæmoglobin, while that of the carbon monoxide compound remains unaltered, or only fades partially.

If a solution of caustic soda of sp. gr. 1.3 be added to normal blood, a black, slimy mass is formed, which, when spread upon a white plate, has a greenish brown color; the same reagent added to blood altered by carbonic oxide forms a firmly clotted mass, which in thin layers upon a white surface is bright red in color.

For the method of detecting and determining carbon monoxide in gaseous mixtures, see p. 244.

Carbon Dioxide.

Carbonic anhydride—Carbonic acid gas—CO_2—exists in small proportion in the atmosphere, and in solution in natural waters. It is formed whenever a substance containing carbon is burned in air or oxygen, and when a carbonate is decomposed by a stronger acid.

It is best obtained by decomposing a natural carbonate, marble or limestone, by a mineral acid—hydrochloric acid.

At ordinary temperatures and pressures it is a colorless gas; produces a sense of suffocation when inhaled; has an acidulous taste; sp. gr. 1.529 at 0°; soluble in an equal volume of water at the ordinary pressure. When subjected to a pressure of thirty-eight atmospheres at 0°, fifty atmospheres at 15°, or seventy-three atmospheres at 30°, it is converted into a transparent, mobile liquid, by whose evaporation, when the pressure is relieved, a degree of cold is produced sufficient to solidify a portion as a snow-like mass, which, by spontaneous evaporation in air, produces a temperature of −90°.

Carbon dioxide neither burns nor does it support combustion; when heated to 1,300°, it is decomposed into carbon monoxide and oxygen; a similar decomposition is brought about by the passage through it of electric sparks. When heated with hydrogen it yields carbon monoxide and water; when potassium, sodium, or magnesium is heated in an atmosphere of carbon dioxide, the gas is decomposed with formation of a carbonate and separation of carbon. When caused to pass through solutions of the hydrates of sodium, potassium, calcium, or barium, it is absorbed, with formation of the carbonates of those elements, which, in the case of the last two, are deposited as white precipitates. Solution of potash is frequently used in analysis to absorb carbon dioxide, and lime and baryta water as tests for its presence. The hydrates mentioned also absorb carbon dioxide from moist air.

Atmospheric carbon dioxide.—Carbon dioxide is a constant constituent of atmospheric air in small and varying quantities; the mean amount in free country air being about four parts in ten thousand. The variations in amount under different conditions is shown in the following table:

AMOUNT OF CARBON DIOXIDE IN AIR.

Collected at	Parts in 10,000.	Determined by
Paris	3.190	Boussingault and Lewy.
Andilly—twenty miles from Paris	2.989	Boussingault and Lewy.
Paris—Day	3.9	Boussingault.
Night	4.2	Boussingault.
Ocean—Day	5.42	Lewy.
Night	3.346	Lewy.
Day	3.011	Thorpe.
Night	2.995	Thorpe.
Geneva	4.68	Saussure.
Meadow—three-fourths mile from Geneva:		
Dry months	4.79 to 5.18	Saussure.
After long rains	3.57 to 4.56	Saussure.
December, damp and cloudy	3.85 to 4.25	Saussure.
January, frost	4.57	Saussure.
January, thaw	4.27	Saussure.
Lake Geneva	4.39	Saussure.
Arctic regions	4.83 to 6.41	Moss.
Gosport barracks	6.45	Chaumont.
Anglesey barracks	14.04	Chaumont.
Hilsey Hospital	4.72	Chaumont.
Portsmouth Hospital	9.76	Chaumont.
Cell in Pentonville Prison	9.89	Chaumont.
Cell in Chatham Prison	16.91	Chaumont.
Boys' school—69 cubic feet per head	31	Roscoe.
Room—51 cubic feet per head	52.8	Weaver.
Girls' school—150 cubic feet per head	72.3	Pettenkofer
Greenhouse—Jardin des Plantes	1.0	
Theatre—Parquet	23.0	
Near ceiling	43.0	
Lead mine—Lamps burn	80.0	F. Leblanc.
Lamps extinguished	390.0	F. Leblanc.
Grotto del Cane	7,360.0	F. Leblanc.

It will be observed that on land the amount is greater by night than by day, while the reverse is the case at sea; on land the green parts of

plants absorb carbon dioxide during the hours of sunlight, but not during those of darkness. The increase in the amount in air over large bodies of water during the day-time is due to the less solubility of carbon dioxide in the surface-water when heated by the sun's rays. The absence of vegetation accounts for the large quantity of carbon dioxide in the air of the polar regions, and the same cause, aided by an increased production, for its excess in the air of cities over that of the country.

The sources of atmospheric carbon dioxide are:

First.—The respiration of animals.—The air expired from the lungs of animals contains a quantity of carbon dioxide, varying with the age, sex, food, and muscular development and activity, while, at the same time, a much smaller quantity is discharged by the skin and in solution in the urine. The following table, from the experiments of Andral and Gavarret, indicates the quantity of carbon dioxide eliminated by males of various ages:

ELIMINATION OF CARBON DIOXIDE.

Age.	Mean weight.		Carbon eliminated, in grams.		Carbon dioxide eliminated, in grams		Oxygen absorbed, in grams.		Carbon dioxide eliminated, in litres.		Oxygen absorbed, in litres.	
	In kilos.	In lbs.	In 1 hour.	In 24 hours.	In 1 hour.	In 24 hours.	In 1 hour.	In 24 hours.	In 1 hour.	In 24 hours.	In 1 hour.	In 24 hours.
8 years	22.26	49.07	5.0	120.8	18.3	442.9	15.613	374.70	9.30	225.16	8.63	207.22
15 years	46.41	102 32	8.7	208.8	31.9	765.6	27.166	651.98	16.21	389.22	18.91	453.89
16 years	53.39	117.70	10.8	259.2	39.6	950.4	33.723	809.36	20.13	483.17	23.48	563.42
18 to 20 years	60.88	134.22	11.4	273.6	41.8	1003.2	35.599	854.32	21.25	510.01	24.78	594.79
20 to 24 years	66.90	147.49	12.2	292.8	44.7	1073.6	38.094	914.28	22.72	545.81	26.52	636.47
40 to 60 years	67.15	148.04	10.1	242.4	37.0	888.8	31.537	756.89	18.81	451.85	21.95	526.92
60 to 80 years	63.35	139.66	9.2	220.8	33.7	809.6	28.727	689.45	17.13	411.59	20.00	479.98

In females the increase of elimination follows the same rule as with males until puberty, when it ceases and the amount exhaled remains about the same until the menopause, when the elimination of carbon dioxide suddenly increases to nearly the same as that occurring in males of the same age, and subsequently gradually declines with advancing age. During pregnancy the elimination of carbon dioxide is temporarily increased. In both sexes and at all ages the exhalation of carbon dioxide is greater during muscular activity than when the individual is at rest, and greater in those whose muscular development is more perfect. An adult man discharges 20.77 litres=three-fourths cubic foot of carbon dioxide per hour, or 498.88 litres=eighteen cubic feet per diem.

The expired air under ordinary conditions contains about 4.5 per cent. by volume of carbon dioxide, the proportion being greater the slower the respiration.

Second.—Combustion.—The greater part of the atmospheric carbon dioxide is a product of the oxidation of carbon in some form as a source of light and heat. In the following table are given the amounts of carbon dioxide produced and of air consumed by different kinds of fuel and illuminating materials; by comparing them with the quantities of the same gases produced and consumed by an adult man it will be seen that in equal times an ordinary gas-burner produces nearly six times as much carbon dioxide and consumes nearly ten times as much air as a man. The

amount of air consumed by fuels is, for practical purposes, greater than that given in the table, as the oxidation is never complete, the air in the chimney frequently containing ten per cent. of oxygen by volume (see below).

COMBUSTION OF FUEL.

Fuel.	Average amount burned in one hour.	Average percentage of		Carbon dioxide produced by				Air deoxidized by				Heat units.	Light in standard candles, 100.
		Carbon.	Hydrogen.	One volume in volumes.	One part by weight in parts by weight.	In one hour. In kilos.	In one hour. In litres.	One volume in volumes.	One kilo in cubic metre.	In one hour. In kilos.	In one hour. In litres.		
Hydrogen	.....	....	100.0	..	....	....	....	2.39	26.89	....	....	34462	..
Carbon to CO_2	.....	100.0	....	..	3.65	....	....	...	9.88	....	....	8080	..
Carbon to CO	.....	100.0	....	..	....	....	....	...	4.93	....	....	2474	..
Carbon monoxide	.....	42.86	....	1.0	1.57	....	....	2.39	0.44	....	....	2403	..
Marsh-gas	.....	75.0	25.00	1.0	2.75	....	....	9.55	13.45	....	....	13063	..
Ethene	.....	85.72	14.28	2.0	3.14	....	....	14.33	12.67	....	....	11857	..
Coal-gas	140 litres	40.0	55.0	0.80	1.67	0.221	112	7.14	11.04	1.293	1000	11000	..
Crude petroleum	.....	84.0	13.0	..	3.08	....	....	...	12.07	....	....	11775	..
Kerosene	15 gr.	87.0	13.0	..	3.17	0.048	25	...	12.12	0.235	182	11055	180
Wax	10 gr.	79.2	13.2	..	2.89	0.029	15	...	11.24	0.146	113	10496	100
Stearic acid	10 gr.	76.05	12.68	..	2.9	0.029	15	...	8.69	0.112	86.9	9716	84
Colza-oil	42 gr.	70.43	10.5	..	2.81	0.118	60	...	8.28	0.450	348	...	159
Wood (dry pine)	.....	39.10	4.90	..	1.43	....	.. ..	...	5.16	...	....	3600	..
Wood charcoal	.....	85.0	....	..	3.10	....	....	...	8 36	....	....	7640	..
Peat	.....	45.0	1.5	..	1.64	....	....	...	4.82	....	....	3000	..
Coke	.....	87.0	....	..	3.17	....	....	...	8.55	....	....	...	..
Anthracite	.....	90.0	2.5	..	3.29	....	....	...	9.22	....	....	6000	..
Alcohol	.....	52.17	13.04	..	1.90	....	....	...	8.64	....	....	7183	..
Adult man	10 gr. C.	....	....	..	....	0.037	19	...	...	0.134	104	...	..

Third.—Fermentation.—Most fermentations, including putrefactive changes, are attended by the liberation of carbon dioxide; thus, alcoholic fermentation takes place according to the equation:

$$\underset{180}{C_6H_{12}O_6} = \underset{92}{2C_2H_6O} + \underset{44}{2CO_2},$$

and consequently discharges into the air forty-four parts by weight of carbon dioxide for every ninety-two parts of alcohol formed, or 191.5 litres of gas for every litre of absolute alcohol obtained.

Fourth.—Tellural sources.—Volcanoes in activity discharge enormous quantities of carbon dioxide, and, in volcanic countries, the same gas is thrown out abundantly through fissures in the earth. All waters, sweet and mineral, hold this gas in solution, and those which have become charged with it under pressure in the earth's crust, upon being relieved of the pressure when they reach the surface, discharge the excess into the air.

Fifth.—Manufacturing processes.—Large quantities of carbon dioxide are added to the air in the vicinity of lime- and brick-kilns, cement-works, etc.

Sixth.—In mines, after explosions of "fire-damp." These explosions are caused by the sudden union of the carbon and hydrogen of CH_4 with the oxygen of the air, and are consequently attended by the formation of large volumes of carbon dioxide, known to miners as *after-damp*.

Constancy of the amount of atmospheric carbon dioxide.—It has been roughly estimated by Poggendorff that 2,500,000,000,000 cubic metres of carbonic acid gas are annually discharged into our atmosphere, and that this quantity represents one eighty-sixth of the total amount at present existing therein. This being the case, with the present production, the percentage of atmospheric carbon dioxide would be doubled in eighty-six years; no such increase has, however, been observed, and the average percentage found by Angus Smith, in 1872, is about the same as that observed by Boussingault in 1840, *i. e.*, four parts in ten thousand. The carbon dioxide discharged into the air is, therefor, removed from it about as fast as it is produced. This removal is effected in two ways: 1st, by the formation of deposits of earthy carbonates by animal organisms, corals, mollusks, etc.; 2d, principally by the process of nutrition of vegetables, which absorb carbon dioxide both by their roots and leaves, and in the latter, under the influence of the sun's rays, decompose it, retaining the carbon, which passes into more complex molecules; and discharging a volume of oxygen about equal to that of the carbonic acid gas absorbed.

Air contaminated with excess of carbon dioxide, and its effects upon the organism.—When, from any of the above sources, the air of a given locality has received sufficient carbon dioxide to raise the proportion above seven parts in ten thousand by volume, it is to be considered as contaminated; the seriousness of the contamination depending not only upon the amount of the increase, but also upon the source of the carbon dioxide. If the gas be derived from fermentation, or from tellural or manufacturing sources, it is simply added to the otherwise unaltered air, and the absolute amount of oxygen present remains the same; when, however, it is produced in a confined space by the processes of combustion and respiration, the composition of the air is much more seriously modified, as not only is there addition of a deleterious gas, but a simultaneous removal of an equal volume of oxygen; hence the importance of providing, by suitable ventilation, for the supply of new air from without to habitations and other places where human beings are collected within doors, especially where the illumination is artificial.

Although an adult man deoxidizes a little over one hundred litres of air in an hour, a calculation of the quantity which he would require in a given time cannot be based exclusively upon that quantity, as the deoxidation cannot be carried to completeness; indeed, when the proportion of carbon dioxide in air exceeds five per cent., it becomes incapable of supporting life, while a much smaller quantity, one per cent., is provocative of severe discomfort, to say the least.

In calculating the quantity of air which should be supplied to a given enclosed space, most authors have agreed to adopt as a basis that the percentage of carbon dioxide should not be allowed to exceed 0.6 volumes per 1,000; of which 0.4 are normally present in air, and 0.2 the product of respiration or combustion. Taking the amount of carbon dioxide eliminated by an adult at 19 litres (=0.7 cubic foot) per hour, a man will have brought the air of an air-tight space of 100 cubic metres (= 3,500 cubic feet) up to the permissible maximum of impurity in an hour. The following table is given by Parkes to indicate the contamination of air

by the respiration of an adult in an hour, and the supply of external air required to restore the proper equilibrium:

Amount of cubic space (breathing-space) for one man in cubic feet.	Ratio per 1,000 of CO_2 from respiration at the end of one hour, if there have been no change of air.	Amount of air necessary to dilute to standard of 0.2, or including initial CO_2, of 0.6 per 1,000 volumes during the first hour.	Amount necessary to dilute to the given standard every hour after the first.
100	6.00	2,900	3,000
200	3.00	2,800	3,000
300	2.00	2,700	3,000
400	1.50	2,600	3,000
500	1.20	2,500	3,000
600	1.00	2,400	3,000
700	0.85	2,300	3,000
800	0.75	2,200	3,000
900	0.66	2,100	3,000
1,000	0.60	2,000	3,000

Practically, owing to the imperfect closing of doors and windows, and to ventilation by chimneys, inhabited spaces are never hermetically closed, and a less quantity of air-supply than that indicated in the table may usually be considered as sufficient.

A sleeping-room occupied by a single person should have a cubic space of 30 to 50 cubic metres (=1,050 to 1,800 cubic feet), conditions which are fulfilled in rooms measuring $10 \times 13 \times 8$ feet, and $13 \times 15.6 \times 9$ feet.

In calculating the space of dormitories to be occupied by several healthy people, the smallest air-space that should, under any circumstances, be allowed, is 12 cubic metres (=420 cubic feet) for each person. To determine the number of individuals that may sleep in a room, multiply its length, width, and height together, and divide the product by 420 if the measurement be in feet, or by 12 if it be in metres. Thus, a dormitory 40 feet long, 20 feet wide, and 10 feet high, is fitted for the accommodation of 19 persons at most, for

$$40 \times 20 \times 10 = 8{,}000 \text{ and } \frac{8{,}000}{420} = 19.05.$$

As a rule, in places where many persons are congregated, it is necessary to resort to some scheme of ventilation by which a sufficient supply of fresh air shall be introduced and the vitiated air removed, the quantity to be supplied varying according to circumstances. Experiment has shown that in order to keep the air pure to the senses the quantity of air which must be supplied per head and per hour in temperate climates are as shown in table on following page. The amounts given are the smallest permissible, and should be exceeded wherever practicable.

Lights.—The amounts of air to be supplied to each individual, given in the last section, are, with the exception of those furnished in mines, based upon the supposition that coal-gas is not used as a means of artificial illumination, or that the burners are so arranged with reference to the ventilating-flues that the products of combustion pass out immediately.

Situation.	Cubic metres.	Cubic feet.
Barracks (day-time	35	1,236
Barracks (night-time)	70	2,472
Workshops (mechanical)	70	2,472
School-rooms	35	1,236
Hospital wards	85	3,002
Hospital wards (surgical)	170	6,004
Contagious and lying-in	170	6,004
Mines, metalliferous	150	5,297
Mines, coal	170	6,004

Each cubic foot of illuminating-gas consumes in its combustion a quantity of oxygen equal to that contained in 7.14 cubic feet of air, and produces 0.8 cubic feet of carbon dioxide, besides a large quantity of watery vapor, and less amounts of sulphuric acid, sulphur dioxide, and sometimes carbon monoxide; and an ordinary gas-burner consumes about three feet per hour. It is obvious, therefor, that a much larger quantity of pure air must be furnished to maintain the atmosphere of an apartment at the standard of 0.6 per 1,000 of carbon dioxide, when the vitiation is produced by the combustion of gas, than when it is the result of the respiration of a human being, and that to such an extent that a single three-foot burner requires a supply of air which would be sufficient for six human beings. As a basis for computation, it may be considered that, for each cubic foot of gas consumed, 1,800 cubic feet of air should be furnished by ventilation.

The contamination of air by gas-lights becomes a question of serious importance in our dwellings upon occasions of social gatherings, and in theatres and other places of public resort which are used during the hours of darkness. The average size of a parlor in a city dwelling is $15 \times 25 \times 15$ feet; it therefor contains 4,875 cubic feet, and its atmosphere would, if it were hermetically closed, be brought to the standard of maximum allowable contamination by the respiration of four adults in an hour, allowing 1,200 cubic feet per head, per hour. If such an apartment be illuminated, upon the occasion of an evening party at which fifty adults are present for four hours, by ten three-feet gas-burners, the amounts of air which should be supplied by ventilation are as follows in cubic feet.

	If the products of combustion of gas be discharged into the room.		If the products of combustion of the gas be carried off.	
	Per hour.	Per hour.	Per hour.	For four hours.
For fifty persons	60,000	240,000	60,000	240,000
For ten gas-burners	54,000	216,000	.....	.....
Totals	114,000	456,000	60,000	240,000

In the first instance, in which the products of the combustion of gas are discharged into the apartment, an adequate ventilation can only be

secured by a complete change of the air every 2.6 minutes, which can only be attained by the use of mechanical contrivances, and with the production of draughts; in the second instance, in which it is presumed that the gas-burners are so situated, with reference to a ventilating-shaft or shafts, that the products of combustion are immediately carried off, not only is the period in which a complete change of air is required extended to 4.8 minutes, but the heat of the burners, causing an uptake current in the ventilator, favors the exit of the vitiated air, and the consequent entrance of external air to take its place.

In theatres the contamination of the air by the burning of gas should be entirely eliminated by placing the burners either under the dome ventilator, or in boxes which open to the air of the house only below the level of the burner, and which are in communication with a ventilating-shaft. Even under these conditions it is necessary, to ensure perfect ventilation, to resort to some mechanical contrivance to remove the air vitiated by respiration and to supply its place by fresh air from without, which may be previously warmed or cooled according to the season, and which, in cities, should be filtered. In a New York theatre, whose ventilation has been carried to such a degree of perfection that the air is sensibly as pure after as before a performance, whose cubical contents are about ninety thousand cubic feet, and whose seating capacity is about six hundred and fifty, there are injected and aspirated by two blowers, one in the cellar and one on the roof, one million to one million two hundred and fifty thousand cubic feet of air per hour, or about one thousand five hundred cubic feet per head per hour.

When artificial illumination is obtained from lamps or candles, or from gas in small quantity and for a short time, the contamination of the air is sufficiently compensated by the ventilation through imperfect closing of the windows. A room without a window should never be used for human habitation.

One important advantage of the electric light, if it ever become practicable, will be that it consumes no oxygen and produces no carbon dioxide.

Although, by the combustion of fuel, oxygen is consumed and carbon dioxide produced, heating arrangements only become a source of vitiation of air under the circumstances detailed above (see p. 235); indeed, in the majority of cases, if properly arranged, they are means of ventilation, either by aspirating the vitiated air of the apartment, or by the introduction of air from without.

Action on the economy.—An animal introduced into an atmosphere of pure carbon dioxide dies almost instantly, and without entrance of the gas into the lungs, death resulting from spasm of the glottis, and consequent apnœa.

When diluted with air, the action of carbon dioxide varies according to its proportion, and according to the proportion of oxygen present.

First.—When the proportion of oxygen is not diminished, the poisonous action of carbon dioxide is not as manifest, in equal quantities, as when the air is poorer in oxygen. An animal will die rapidly in an atmosphere composed of twenty-one per cent. O, fifty-nine per cent. N, and twenty per cent. CO_2 by volume; but will live for several hours in an atmosphere whose composition is forty per cent. O, thirty-seven per cent. N, twenty-three per cent. CO_2. If carbon dioxide be added to normal air, of course the relative quantity of oxygen is slightly diminished, while its absolute quantity remains the same; this is the condition of affairs existing in

nature when the gas is discharged into the air; under these circumstances an addition of ten to fifteen per cent. of CO_2 renders an air rapidly poisonous, and one of five to eight per cent. will cause the death of small animals more slowly. Even a less proportion than this may become fatal to an individual not habituated.

In the higher states of dilution, carbon dioxide produces immediate loss of muscular power, and death without a struggle; when more dilute, a sense of irritation of the larynx, drowsiness, pain in the head, giddiness, gradual loss of muscular power, and death in coma.

Second.—If the carbon dioxide present in air be produced by respiration or combustion, the proportion of oxygen is at the same time diminished, and much smaller absolute and relative amounts of the poisonous gas will produce the effects mentioned above; thus, an atmosphere containing in volumes 19.75 per cent. O, 74.25 per cent. N, six per cent. CO_2, is much more rapidly fatal than one composed of twenty-one per cent. O, fifty-nine per cent. N, twenty per cent. CO_2. With a corresponding reduction of oxygen, five per cent. of carbon dioxide renders an air sufficiently poisonous to destroy life; two per cent. produces severe suffering; one per cent. causes great discomfort, while 0.1 per cent., or even less, is recognized by a sense of closeness.

The *treatment* in all cases of poisoning by carbon dioxide consists in the inhalation of pure air (to which a small excess of oxygen may be added), aided, if necessary, by artificial respiration, the cold douche, galvanism, and friction.

When it chances that an individual entering an atmosphere containing an excess of carbon dioxide, or other noxious gas, is seen to fall insensible, it is simply multiplying the number of victims, for others to follow, unprotected, with a view to effecting a rescue. Probably the most readily obtainable protection is a towel saturated with lime-water, and so held over the mouth and nostrils that the inspired air passes through it, and also through two or three layers of dry towelling interposed between the moistened part and the skin. Obviously this protection will not be efficacious for a long time, and in situations where such accidents are liable to occur, as in mines, fermenting cellars, etc., it cannot be too strongly recommended that there be kept at hand air-pumps, tubing, and helmets, such as are used by divers, but of lighter construction, to be used by the rescuers upon such occasions.

Detection of carbon dioxide and analysis of confined air.—Carbon dioxide, or air containing it, causes a white precipitate when caused to bubble through lime or baryta water; normal air contains enough of the gas to form a scum upon the surface of these solutions when exposed to it.

It was at one time supposed that air in which a candle continued to burn was also capable of maintaining respiration. This is, however, by no means necessarily true; a candle introduced into an atmosphere in which the normal proportion of oxygen is contained, burns readily in the presence of eight per cent. of carbon dioxide; is perceptibly dulled by ten per cent.; is usually extinguished with thirteen per ceut.; always extinguished with sixteen per cent. Its extinction is caused by a less proportion of carbon dioxide, four per cent., if the quantity of oxygen be at the same time diminished. Moreover, a contaminated atmosphere may not contain enough carbon dioxide to extinguish, or perceptibly dim the flame of a candle, and at the same time contain enough of the monoxide to render it fatally poisonous if inhaled.

The presence of carbon dioxide in a gaseous mixture is determined by

its absorption by a solution of potassium hydrate; its quantity either by measuring the diminution in bulk of the gas, or by noting the increase in weight of the alkaline solution.

To determine the proportions of the various gases present in air, it is made to pass through a series of tubes which have been previously weighed: 1st, through a U-shaped tube containing fragments of pumice-stone, saturated with sulphuric acid; by the increase in weight of this tube the amount of watery vapor is determined; 2d, through a Liebig's bulb-apparatus, filled with a solution of potassium hydrate. The rapidity of the current should be so regulated that about thirty bubbles a minute pass through this apparatus; 3d, through a U-tube filled with fragments of pumice saturated with sulphuric acid. Numbers two and three are weighed together, the increase in their weight is the weight of CO_2 in the volume of air drawn through the apparatus; every gram of increase in weight represents 0.50607 litre, or 31.60356 cubic inches.

The arrangement of the remainder of the absorption apparatus differs according to whether carbon monoxide and marsh-gas, or oxygen, is to be determined. In the former case the air is next passed; 4th, through a tube of difficultly fusible glass, filled with black oxide of copper, and heated to redness, in which the gases mentioned are converted into water and carbon dioxide; then 5th, through a U-tube filled with pumice, moistened with sulphuric acid, whose increase of weight indicates the amount of water so formed. Every gram of increase of weight in this tube represents 0.444 gram, or 0.621 litre, or 38.781 cubic inches of marsh-gas. Finally, the gas is passed, 6th, through a carbon dioxide apparatus, similar to numbers two and three, from whose increase in weight the quantity of carbon monoxide is calculated, thus: first, 2.75 grams are deducted for each gram of marsh-gas found by number five; of the remainder, every gram represents 0.6364 grams, or 0.5085 litre, or 31.755 cubic inches of carbon monoxide.

If the percentage of oxygen is to be determined, the gas, after passing from No. 3, is collected in a graduated tube and its volume measured; a concentrated solution of potassium pyrogallate is passed into the tube, which is agitated without removing its opening from the trough, allowed to stand, and the volume again determined; the difference in volume is the quantity of oxygen in the original volume of air. In both measurements the level of liquid in the tube must be the same as that in the trough.

To draw the air through the absorbing apparatus, an aspirator is used, and the volume of air determined by the volume of escaping water.

Sulphocarbonic Acid, $CS\langle^{SH}_{SH}$,

is of interest as corresponding in constitution to the hypothetical carbonic acid, sulphur replacing oxygen, but, unlike that acid, being capable of existing free. It may be obtained by treating an alkaline sulphocarbonate with hydrochloric acid and immediately afterward with water, as a reddish brown oily liquid, which is insoluble in water, and readily decomposable into carbon disulphide and hydrogen sulphide.

Carbon Disulphide.

Bisulphide of carbon, CS_2.—This substance, which bears the same relation to sulphocarbonic acid and the sulphocarbonates that carbon dioxide does to the hypothetical carbonic acid and to the carbonates, does not exist in nature. It is obtained by passing the vapor of sulphur over carbon heated to redness, and partially purified by rectification. It is further purified by agitation and twenty-four hours' contact with one-half per cent. of powdered mercuric chloride, decantation, treatment with two per cent. of an odorless fatty material, and slow distillation.

The pure product is a colorless liquid, which has a peculiar, but not disagreeable, ethereal odor; the nauseating odor of the commercial bisulphide is due to the presence of another sulphuretted body; boils at 47°; sp. gr. 1.293; very volatile; its rapid evaporation in vacuo produces a temperature of −60°; it does not mix with water, through which it falls in globular drops. It refracts light strongly, and is used to fill prisms used in some forms of spectroscopic apparatus.

It is highly inflammable, and burns with a bluish flame, giving off carbon dioxide and sulphur dioxide; its vapor forms highly explosive mixtures with air, which detonate on contact with a glass rod heated to 250°. Its vapor forms a mixture with nitrogen dioxide, which, when ignited, burns with a brilliant flame, rich in actinic rays.

There also exists a substance intermediate in composition between carbon dioxide and carbon disulphide, known as *carbon oxysulphide*, CSO, which is an inflammable, colorless gas, obtained by decomposing potassium sulphocyanate with dilute sulphuric acid.

Carbon disulphide is now manufactured in large quantities, and is used in the arts to dissolve the ordinary phosphorus, remaining as an impurity in the preparation of the red variety, as a solvent of sulphur and india-rubber, and for the extraction of fats and oils, which it dissolves freely.

Toxicology.—Cases of acute poisoning by carbon disulphide have hitherto only been observed in animals; its action is very similar to that of chloroform.

Workmen engaged in the manufacture of carbon disulphide and in the vulcanization of rubber, as well as others exposed to the vapor of the disulphide, are subject to a form of chronic poisoning which may be divided into two stages. The first, or stage of excitation, is marked by headache, vertigo, a disagreeable taste, cramps in the legs; the patient talks, laughs, sings, and weeps immoderately, and sometimes becomes violently delirious. In the second stage the patient becomes sad and sleepy, sensibility diminishes sometimes to the extent of complete anæsthesia, especially of the lower extremities, the headache becomes more intense, the appetite is greatly impaired, and there is general weakness of the limbs, which terminates in paralysis.

The only remedy which has been suggested is through ventilation of the workshops and abandonment of the trade at the first appearance of the symptoms.

Glycollic Acid, $\begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}$,

is formed by the oxidation of glycol, by the action of nitrous acid upon glycocol, and by the action of potassium hydrate upon monochloracetic acid.

It forms deliquescent, acicular crystals; very soluble in water; soluble in alcohol and ether; has a strongly acid taste and reaction; fuses at 78°; is decomposed at 150°; at an intermediate temperature it loses H_2O, forming *glycollide*, or *glycollic anhydride*, $C_2H_2O_2$.

It is a monobasic acid. The hydrogen of the group CH_2OH may be replaced by an alcoholic radical to form other acids, such as amylglycollic acid, $\begin{matrix} CH_2O,C_5H_{11} \\ | \\ COOH \end{matrix}$.

Lactic Acids, $C_3H_6O_3$.

There are probably three, certainly two, acids having this composition, which differ from each other mainly in the products of their decomposition, in their physical properties, and in the solubility and amount of water of crystallization of their salts. They resemble each other in being colorless, syrupy liquids; insoluble in water, alcohol, and ether, and very acid in taste and in reaction.

Two of these acids would seem, from their products of decomposition, to be of similar constitution, while the molecular composition of the third is distinct; the two of similar composition are sometimes designated as *ethylidene lactic acids*, because of their containing the group of atoms CH_3, while the third is designated as *ethyleno-lactic acid*, as it contains the group CH_2; the composition is expressed by the formulæ:

$$\begin{matrix} CH_3 \\ | \\ CH,OH \\ | \\ COOH \end{matrix}$$

Ethylidene lactic acid.

$$\begin{matrix} CH_2OH \\ | \\ CH_2 \\ | \\ COOH \end{matrix}$$

Ethyleno-lactic acid.

Obviously it is the ethylene acid which is the superior homologue of glycollic acid.

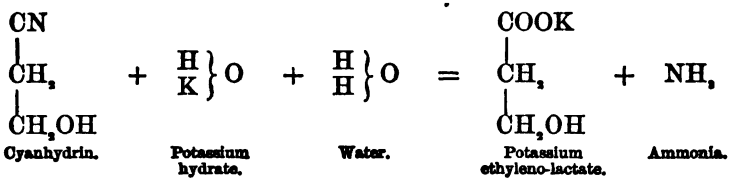
Ethyleno-lactic acid.—As early as 1807 Berzelius discovered in muscular tissue an acid which he took to be lactic acid, but which was subsequently shown by Liebig to differ from it in several of its characters. The latter chemist suggested the name of *sarcolactic acid*, which it has retained until recent researches have shown that the name must be abandoned, as the acid in question is a mixture of two distinct acids—ethyleno-lactic and optically active ethylidene lactic acid—both of which differ from the ordinary lactic acid of fermentation.

Ethyleno-lactic acid may be obtained from muscular tissue, or better, from Liebig's extract of meat, by a process described below (see p. 248). It may also be obtained synthetically by a process which indicates its constitution and the rationale of its name. By the action of potassium cyanide upon ethylene chlorhydrate, the nitrite of the ethyleno-lactic acid is formed:

$$\begin{matrix} CH_2,Cl \\ | \\ CH_2,OH \end{matrix} + \left.\begin{matrix} CN \\ K \end{matrix}\right\} = \begin{matrix} CH_2-CN \\ | \\ CH_2-OH \end{matrix} + \left.\begin{matrix} Cl \\ K \end{matrix}\right\}$$

Ethylene chlorhydrate. | Potassium cyanide. | Cyanhydrin. | Potassium chloride.

The cyanhydrine so obtained, when acted upon by caustic potassa, is decomposed with elimination of ammonia and formation of potassium ethyleno-lactate:



It is distinguished by the following characters: it is optically inactive, as are also solutions of its salts; its zinc salt contains two molecules of water of crystallization, and is very soluble in water and quite soluble in alcohol. When oxidized by chromic acid this acid yields malonic acid, as would be expected from an examination of the formulæ of the two acids:



Of the two ethylidene lactic acids, that which is *optically active* is the one accompanying ethylene lactic acid, and predominating over it in amount in dead muscle; it is to this acid that the name *paralactic acid* is most properly applied.

It may be obtained from Liebig's meat extract; this is dissolved in four parts water; eight parts strong alcohol are then added during constant agitation; after standing, the clear liquid is decanted off, and the insoluble residue again extracted with two parts of warm water, and the solution precipitated with four parts strong alcohol. The united alcoholic fluids are evaporated to a thin syrup over the water-bath, and the residue again precipitated with four volumes of strong alcohol; the clear alcoholic fluid is evaporated to dryness; the residue extracted with water; the solution acidulated with dilute sulphuric acid and shaken with successive portions of ether. The ethereal fluid, on evaporation, leaves a mixture of this acid and ethyleno-lactic acid, which is dissolved in water; the solution is boiled with zinc oxide, filtered, the filtrate evaporated until crystals begin to form, when four or five volumes of strong alcohol are added and the mixture set aside; zinc paralactate crystallizes at first, and is thus separated from the ethyline lactate, which is much more soluble. From the zinc salts the acids are obtained by solution in water, decomposition by hydrogen sulphide, filtration, concentration, extraction with ether, and evaporation of the ethereal solutions.

Paralactic acid differs from its two isomeres in that its solutions are dextrogyrous, and the solutions of its salts are lævogyrous. The specific rotary power of the acid is $[a]_D = +3.5°$; that of the zinc salt $[a]_D = -7.6°$; and of the calcium salt $[a]_D = -3.8°$.

Its products of decomposition are the same as those of ordinary lactic acid.

Ordinary lactic acid—Lactic acid of fermentation—Optically inactive ethylidene lactic acid—exists in nature, widely distributed in the vegetable kingdom, and, as its name implies, as the product of a fermentation which is designated as the lactic, in milk, sour-krout, fermented beet-juice, and rice, and in the liquid refuse of starch-factories and tanneries.

Lactic acid is obtained as a product of the fermentation of certain sugars, milk-sugar and grape-sugar, as a result of the processes of nutrition of a minute vegetable, the lactic ferment, in which the sugar is converted into its polymere:

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Lactic acid.}}{2C_3H_6O_3}$$

The process usually followed consists in allowing a solution composed of cane-sugar, 3 kilos, tartaric acid, 15 grams, water, 13 kilos, to stand several days; 60 grams of rotten cheese, mixed with 4 kilos skimmed milk and 1½ kilos washed chalk, are then added, and the mass exposed to a temperature of 30°—35° for ten days, being stirred from time to time; 10 kilos of boiling water and 15 grams of slacked lime are then added; the liquid is filtered through a cloth, concentrated, and allowed to crystallize; the calcium lactate so obtained, purified by recrystallization, is dissolved in water and decomposed by an equivalent quantity of sulphuric acid; the clear watery fluid is neutralized with zinc carbonate. The zinc lactate so formed is purified by recrystallization, decomposed with hydrogen sulphide, and the liberated lactic acid separated by filtration and concentration of the watery liquid.

It has also been obtained synthetically by oxidation of the propylglycol of Wurtz, which is a secondary glycol, a synthesis which indicates its constitution:

$$\underset{\text{Propylglycol.}}{\begin{matrix}CH_3\\|\\CHOH\\|\\CH_2OH\end{matrix}} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Lactic acid.}}{\begin{matrix}CH_3\\|\\CHOH\\|\\COOH\end{matrix}} + \underset{\text{Water.}}{H_2O}$$

It is a colorless, syrupy liquid; sp. gr. 1.215 at 20°; does not solidify at —24°; soluble in water, alcohol, and ether; is not capable of distillation without decomposition; when heated to 130° it loses water and is converted into *dilactic acid*, $C_6H_{10}O_5$, and, when heated to 250°, into *lactide*, $C_3H_4O_2$. It is a good solvent of tricalcic phosphate.

Oxidizing agents convert this acid into formic and acetic acids without the formation of any malonic acid.

Physiological.—The three lactic acids are widely disseminated in animal nature, either free or in combination. Free lactic acid of fermentation occurs in the contents of the small intestine, and, when vegetable food has been taken, in the stomach; it is not, however, the acid to which the *normal, unmixed* gastric juice owes its acidity. Its salts have been found to exist in the contents of the stomach and those of the intestines, chyle, bile, parenchymatous fluid of spleen, liver, thymus, thyroid, pancreas, lungs, and brain; urine. Pathologically in the blood in leucocythæmia, pyæmia, puerperal fever, and after excessive muscular effort; in

the fluids of ovarian cysts and transudations. In the urine it is abundant in phosphorus-poisoning, in acute atrophy of the liver, and in rachitis and osteomalachia.

Muscular tissue, after death or continued contractions, contains the mixture of acids known to the older authors as sarcolactic acid. Normal, quiescent muscle is neutral in reaction; but, as soon as rigor mortis appears, or if the muscle be tetanized, its reaction becomes acid from the liberation of sarcolactic acid. Whether these acids are formed *de novo* during the contraction of the muscle, or whether they are produced by the decomposition of lactates existing in the quiescent muscle, is still undetermined; certain it is, however, that a given quantity of muscle has, when separated from the circulation, a fixed maximum of acid-producing capacity, which is greater in a muscle that has been tetanized during the interval between its removal and the establishment of rigor, than in one which has been at rest.

There exist no grounds upon which to base the supposition that, in rheumatic fever, lactic acid is present in the blood.

The remaining acids of this series are not of sufficient practical interest to warrant further consideration.

DIATOMIC AND DIBASIC ACIDS.

Series $C_nH_{2n-2}O_4$.

The acids of this series at present known are:

Oxalic acid.....$C_2O_4H_2$	Adipic acid .....$C_6O_4H_{10}$	Azelaic acid.....$C_9O_4H_{16}$
Malonic acid.....$C_3O_4H_4$	Pimelic acid .....$C_7O_4H_{12}$	Sebacic acid.....$C_{10}O_4H_{18}$
Succinic acid.....$C_4O_4H_6$	Suberic acid .....$C_8O_4H_{14}$	Roccellic acid.....$C_{17}O_4H_{32}$
Deoxyglutanic acid . $C_5O_4H_8$		

They are derived from the primary glycols by complete oxidation; they are diatomic and dibasic, and contain two groups, CO, OH. They form two series of salts with the univalent metals, and two series of ethers, one of which contains neutral, and the other acid ethers. They may be obtained from the corresponding glycols, or acids of the preceding series, by oxidation.

Oxalic Acid, $\begin{matrix}CO,OH\\|\\CO,OH\end{matrix}$,

exists in the oxalates of potassium, sodium, calcium, magnesium, and iron; in the juices of many plants, notably in sorrel, rhubarb, cinchona, oak, etc.; as a native ferrous oxalate—humboldtine; and in small quantity in human urine.

It was formerly obtained from the vegetables in which it exists, but is now artificially prepared, either by oxidizing sugar or starch by nitric acid, or by the action of an alkaline hydrate in a state of fusion upon sawdust, by which an alkaline oxalate is produced. The soluble alkaline salt is converted into the insoluble calcium or lead oxalate, which is washed and decomposed with an equivalent quantity of sulphuric acid or

with hydrogen sulphide; the liberated oxalic acid is purified by recrystallization. The product so obtained is sufficiently pure for industrial purposes, but is still contaminated with small quantities of potassium sulphate and oxalate, and calcium oxalate, to separate which, when the acid is required pure, as for volumetric analysis, the commercial acid is repeatedly recrystallized from water and from alcohol.

Oxalic acid is also formed in a number of other reactions: by the oxidation of many organic substances—alcohol, glycol, sugar, etc.; by the action of potassa in fusion upon the alkaline formiates; and by the action of potassium or sodium upon carbon dioxide.

It crystallizes in transparent prisms, containing two molecules of water of crystallization, which effloresce on exposure to air, and lose their water slowly but completely at 100°, or in a dry vacuum. It fuses at 98° in its water of crystallization; at 110°—132° it sublimes in the anhydrous form, while a portion is decomposed; above 160° the decomposition is more extensive; water, the two oxides of carbon and formic acid, are produced, while a portion of the acid is sublimed unchanged. It dissolves in 15.5 parts of water at 10°; in 9.5 parts at 14°, and in a smaller quantity of boiling water; the presence of nitric acid increases its solubility. It is quite soluble in alcohol. It has a sharp taste and an acid reaction in solution.

Oxalic acid is quite readily oxidized; in watery solution it is converted into carbon dioxide and water, slowly by simple exposure to air, more rapidly, in the presence of platinum black or of the salts of platinum and gold, under the influence of sunlight, or when heated with nitric acid, manganese dioxide, chromic acid, bromine, chlorine, or hypochlorous acid. Its oxidation, when it is triturated dry with pure oxide of lead, is sufficiently active to heat the mass to redness. Sulphuric and phosphoric acids and other dehydrating agents decompose it into water and the two oxides of carbon.

Oxalic acid, or the soluble oxalates, in neutral or alkaline solution, gives a white precipitate of calcium oxalate with any soluble calcium salt. The oxalates of silver and lead, and mercurous oxalate, are also insoluble or very sparingly soluble in water.

Uses.—Oxalic acid is largely used in the arts, in dyeing and calico printing; to clean copper utensils; and to remove stains of iron-rust or of ink. It was at one time used in medicine, but its use has been abandoned.

Toxicology.—Although certain oxalates are constant constituents of vegetable food and of the human body, the acid itself, as well as hydropotassic oxalate, is a violent poison when taken internally, acting both locally as a corrosive upon the tissues with which it comes in contact, and as a true poison, the predominance of either action depending upon the concentration of the solution. Dilute solutions may produce death without pain or vomiting, and after symptoms resembling those of narcotic poisoning. Death has followed a dose of ʒ j. of the solid acid, and recovery a dose of ℥ j. in solution. When death occurs, it may be almost instantaneously, usually within half an hour; sometimes after weeks or months, from secondary causes.

The treatment, which must be as expeditious as possible, consists in the administration, *first*, of lime or magnesia, or a salt of calcium or magnesium suspended or dissolved in a *small* quantity of water or mucilaginous fluid; afterward, if vomiting have not occurred spontaneously, and if the symptoms of corrosion have not been severe, an emetic may be given. In the treatment of this form of poisoning several points of nega-

tive caution are to be observed. As in all cases in which a corrosive has been taken internally, the use of the stomach-pump is to be avoided. The alkaline carbonates, which may be used as antidotes when the mineral acids have been ingested, are of no value in cases of oxalic acid poisoning, as the oxalates which they form are soluble, and almost as poisonous as the acid itself. The ingestion of water, or the administration of warm water as an emetic, is contraindicated when the poison has been taken in the solid form (or where doubt exists as to what form it was taken in), as they dissolve, and thus favor the absorption of the poison.

Analysis.—In fatal cases of poisoning by oxalic acid the contents of the stomach are sometimes strongly acid in reaction; more usually, owing to the administration of antidotes, neutral, or even alkaline. In a systematic analysis the poison is to be sought for in the residue of the portion examined for prussic acid and phosphorus; or, if the examination for those substances be omitted, in the residue or final alkaline fluid of the process for alkaloids (see p. 348 *et seq.*). If oxalic acid alone is to be sought for, the contents of the stomach, or other substances *if acid*, are extracted with water, the liquid filtered, the filtrate evaporated, the residue extracted with alcohol, the alcoholic fluid evaporated, the residue redissolved in water (solution No. 1). The portion undissolved by alcohol is extracted with alcohol acidulated with hydrochloric acid, the solution evaporated after filtration, the residue dissolved in water (solution No. 2). Solution No. 1 contains any oxalic acid which may have existed free in the substances examined; No. 2 that which existed in the form of *soluble* oxalates. If lime or magnesia have been administered as an antidote, the substances must be boiled for an hour or two with potassium carbonate (not the hydrate), filtered, and the filtrate treated as above. In the solutions so obtained, oxalic acid is characterized by the following

Tests.—Silver nitrate forms a white precipitate, readily soluble in nitric acid and in ammonia. The precipitate does not darken when the fluid is boiled, but, when dried and heated on platinum foil, it explodes. Lime-water or solution of calcium chloride or sulphate, form a white precipitate, insoluble in water, almost so in acetic and oxalic acid; readily soluble in hydrochloric or nitric acid. The formation of this precipitate in dilute solutions is favored by a previous addition of ammonium hydrate.

Lead acetate, in not too dilute solutions, produces a white precipitate, soluble in nitric, insoluble in acetic acid.

In toxical analyses it must not be forgotten that small quantities of oxalates may be introduced into the stomach as normal constituents of the food.

In cases of suspected poisoning by oxalic acid, the urine should be examined microscopically for crystals of calcium oxalate.

Malonic Acid, $\begin{matrix} CO,OH \\ | \\ CH_2 \\ | \\ CO,OH \end{matrix}$,

is of interest as a product of oxidation of the corresponding acid of the preceding series, ethyleno-lactic acid, and as being identical with an acid obtained from tobacco, and designated as *nicotic acid.*

It crystallizes in prismatic needles; which fuse at 140°, are decomposed at 150°; and are very soluble in water, alcohol, and ether.

Succinic Acid, $\begin{matrix} CH_2—CO,OH \\ | \\ CH_2—CO,OH \end{matrix}$,

was one of the first organic acids known to chemists. It exists in nature in amber, coal, fossil wood, and in small quantities in animal and vegetable tissues. Its presence has been detected in the normal urine after the use of fruits and of asparagus, in the parenchymatous fluids of the spleen, thyroid, and thymus, and in the fluids of hydrocele and of hydatid cysts. It is also formed in small quantity during alcoholic fermentation. It is formed as a product of oxidation of many fats and fatty acids; and by synthesis from ethylene cyanide.

It may be obtained by dry distillation of amber, or, preferably, by the fermentation of malic acid. One kilo of calcic malate is dissolved in three kilos of water, and to the solution eighty grams of stale cheese, or 250 c.c. of yeast, are added. The mass is exposed to a temperature of 30°—40°, for five to six days, when succinic acid is formed according to the equation:

$$\underset{\text{Malic acid.}}{3C_4H_6O_5} = \underset{\text{Succinic acid.}}{2C_4H_6O_4} + \underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Carbon dioxide.}}{2CO_2} + \underset{\text{Water.}}{H_2O}$$

A mixture of calcium succinate and carbonate crystallizes out, is washed, sulphuric acid added as long as effervescence occurs, the mass extracted with water, sulphuric acid added as long as a precipitate is formed, the solution filtered, and the succinic acid allowed to crystallize out.

It crystallizes in large prisms or hexagonal plates, which are colorless, odorless, permanent in air, acid in taste, soluble in water, sparingly so in ether and in cold alcohol. It fuses at 180°, and distils with partial decomposition at 235°.

Succinic acid withstands the action of oxidizing agents; reducing agents convert it into the corresponding acid of the fatty series, butyric acid; with bromine it forms products of substitution; sulphuric acid is without action upon it; phosphoric anhydride removes the elements of a molecule of water and converts it into *succinic anhydride*, $C_4H_4O_3$.

The remaining acids of this series may be dismissed with a few words.

Deoxyglutanic acid, $C_5H_8O_4$—is derived from glutanic acid by heating with hydriodic acid. It forms large crystals, soluble in water. It is isomeric with pyrotartaric acid.

Adipic acid, $C_6H_{10}O_4$—is formed by the action of nitric acid upon many fatty substances; it bears the same relation to leucic acid that oxalic does to glycolic acid. It is soluble in water, alcohol, and ether; fuses at 130°.

Pimelic acid, $C_7H_{12}O_4$—is another product of the oxidation by nitric acid of fatty substances, notably of oleic acid. It forms small crystals; sparingly soluble in water, alcohol, and ether; quite soluble in the same liquids when hot.

Suberic acid, $C_8H_{14}O_4$—a product of the oxidation, by nitric acid, of cork, oleic, and stearic acids, and oils containing them. It forms small

crystals, sparingly soluble in cold water, readily soluble in hot water, alcohol, and ether.

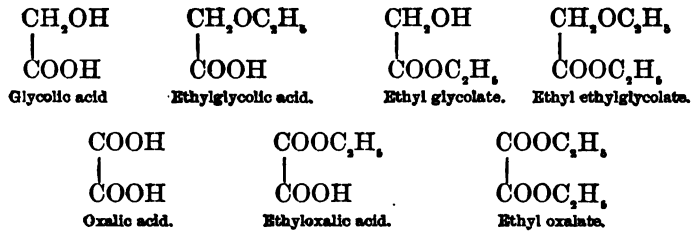
Azelaic acid, $C_9H_{16}O_4$—also known as *anchoic acid*, is formed, along with the preceding, by oxidation of castor-oil.

Sebacic acid, $C_{10}H_{18}O_4$—is a product of the decomposition of oleic acid by dry distillation, and of the action of potash on castor-oil. It crystallizes in pearly needles; fusible at 126°; sparingly soluble in cold water, readily soluble in hot water, alcohol, and ether.

Roccellic acid, $C_{17}H_{32}O_4$—exists in various lichens, *roccella tinctoria*, *fuciformis*, *etc.*, from which *litmus* and *orchel* are prepared. It crystallizes in colorless crystals; fusible at 132°; insoluble in water; soluble in alcohol and in ether.

COMPOUND ETHERS OF THE ACIDS OF THE SERIES $C_nH_{2n}O_2$ AND $C_nH_{2n-2}O_4$.

The members of both of these series contain two atoms of hydrogen replaceable by alcoholic radicals. In those of the series $C_nH_{2n}O_2$, with the exception of carbonic acid, being monobasic, although diatomic, it is not immaterial which hydrogen is so replaced; if it be that of the group CH_2OH, the resulting compound is a monobasic acid, in which the hydrogen of the group COOH may be replaced by another alcoholic radical to form a neutral ether of the new acid; if, on the other hand, the hydrogen of the group COOH be first replaced, a neutral compound ether is formed. In the members of the series $C_nH_{2n-2}O_4$, which are dibasic, the substitution of an alcoholic radical for the hydrogen of either group COOH produces a monobasic acid, in which the hydrogen of the other COOH may be replaced by another radical to form a neutral ether. The following formulæ indicate the differences in the nature of these compounds:

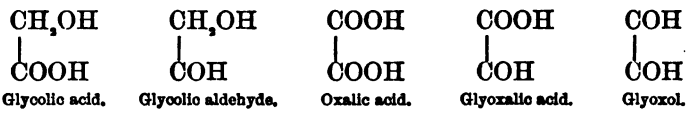


None of the many ethers of these series are of medical interest.

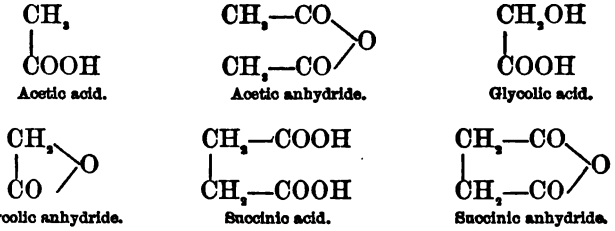
ALDEHYDES AND ANHYDRIDES OF THE SERIES $C_nH_{2n}O_2$ AND $C_nH_{2n-2}O_4$.

In treating of the monoatomic compounds, it was stated that substances existed corresponding to the fatty acids, known as aldehydes and anhydrides, the former differing from the acids in that they contained the group COH instead of COOH, the latter being the oxides of the acid radicals. Similar compounds exist corresponding to the acids of these two series.

The aldehydes corresponding to the series $C_nH_{2n}O_3$ contain the group COH in place of the group COOH, and as they also contain the group CH_2OH, they are possessed of the double function of primary alcohol and aldehyde. Those of the series $C_nH_{2n-2}O_4$ form two series; in one of which only one of the groups COOH is deoxidized to COH; in the other, both. Those of the first series, still containing a group COOH, are monobasic acids as well as aldehydes:



While the anhydrides of the fatty series may be considered as derived from the acids by the subtraction of the elements of a molecule of water from two molecules of the acids, those of both the series of acids under consideration are derived from a single molecule of the acid by the subtraction of the elements of a molecule of water:



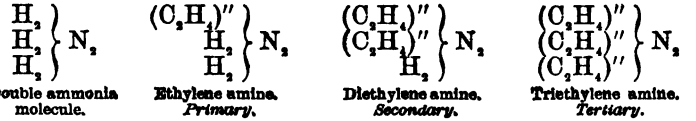
None of those substances are of practical medical importance.

AMINES OF THE GLYCOLS.

Ethylenic Compound Ammonias.

These substances are derived from a double molecule of ammonia, or of ammonium hydrate, by the substitution of the diatomic radicals of the glycols (hydrocarbons of the series C_nH_{2n}) for an equivalent number of hydrogen atoms. They are distinguished from the corresponding compounds of the radicals of the monoatomic alcohols, the *monamines*, by the designation of *diamines*.

When it is considered that in the formation of these substances double hydrogen atoms can be replaced by diatomic radicals to form primary, secondary, and tertiary amines:



that others exist in which two univalent radicals replace a divalent radical; others, again, in which atoms of hydrogen have been replaced by groups OH; and finally, that similar compounds of phosphorus, arsenic,

and antimony exist, it is not astonishing that the study of the vast number of substances, the possibility of whose existence is thus indicated, is still in its infancy.

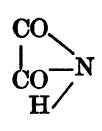
Although at present we know of none of these substances which is of medical interest, there is strong probability that further investigation will show some of the natural alkaloids, whose constitution is as yet unknown, to belong in this class.

AMIDES OF THE ACIDS OF THE SERIES

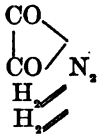
$C_nH_{2n}O_2$ AND $C_nH_{2n-2}O_4$.

This class of substances, formed by the substitution of radicals of the acids for atoms of hydrogen in ammonia molecules, contains some substances of the greatest medical interest. The radicals of the acids of the series $C_nH_{2n}O_2$, except carbonic acid, being univalent, form amides similar in constitution to those of the acids of the series $C_nH_{2n}O_2$ (p. 207).

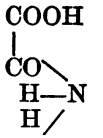
In the case of the dibasic acids no less than three series of amides are known to exist; thus we have, corresponding to oxalic acid:



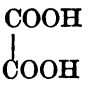
Oximide.
Secondary monamide.



Oxamide.
Primary diamide.



Oxamic acid.
Primary monamide.



Oxalic acid.
Acid.

In the first of these, two atoms of hydrogen of a single molecule of ammonia are replaced by the divalent radical of the acid; these are distinguished as *imides*. Those of the second series are normally formed *diamides*. In the third series, the univalent remainder, left by the removal of OH from the acid, replaces an atom of hydrogen in one molecule of ammonia, and the resulting compound, still containing a group COOH, has the functions of a monobasic acid.

Amides of Carbonic Acid.

Carbimide, $(CO)''_{H}\rangle N$.

Although many chemists have regarded cyanic acid (*q. v.*) as being the imide of carbonic acid, there are many reasons, drawn from the methods of formation and properties of cyanic acid, which lead us to assign to it the constitution $\begin{matrix} CN \\ | \\ OH \end{matrix}$, rather than that given above, and to consider it as the isomere of the hitherto undiscovered carbimide.

Carbamide—Urea, $\left.\begin{matrix}(CO)''\\ H_2\\ H_2\end{matrix}\right\}N_2$.

This important substance, whose existence was suspected by Boerhaave and Haller, was first obtained in an impure form by the younger Rouelle, in 1771, who called it *extractum saponaceum urinæ;* and in a state of comparative purity by Cruikshank in 1798. The name *urea* was given it in 1799, by Fourcroy and Vauquelin. It is of great interest, historically as well as medically, as being the first in the great catalogue of organic substances that have been obtained by synthetic methods, its synthesis having been effected by Woehler in 1828.

Urea does not occur in the vegetable world; it exists principally in the urine of man and of the mammalia; also in smaller quantity in the excrements of birds, fishes, and some reptiles; in the human and mammalian blood, chyle, lymph, liver, spleen, lungs, brain, vitreous and aqueous humors, saliva, perspiration, bile, milk, amniotic and allantoic fluids, muscular tissue, and in serous fluids (see below).

Urea is formed in a number of reactions:

First.—As a product of decomposition of uric acid in various ways.

Second.—By the oxidation of oxamide.

Third.—By the action of caustic potassa, and of other reagents upon creatin, sarcosine being formed at the same time:

$$\underset{\text{Creatin.}}{C_4H_9N_3O_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Urea.}}{CON_2H_4} + \underset{\text{Sarcosine.}}{C_3H_7NO_2}.$$

Fourth.—By the limited oxidation of albuminoid substances by potassium permanganate (see below).

Fifth.—By the molecular transformation of its isomeride, ammonium cyanate:

$$\underset{\text{Ammonium cyanate.}}{\begin{matrix}CN\\ |\\ ONH_4\end{matrix}} = \underset{\text{Urea.}}{\left.\begin{matrix}(CO)\\ H_2\\ H_2\end{matrix}\right\}N_2}$$

This is a step in the classical method of synthesis of Woehler, and of the process now used for the preparation of urea artificially.

Sixth.—By the action of carbon oxychloride upon dry ammonia.

Seventh.—By the action of ammonium hydrate on ethyl carbonate at 180°.

Eighth.—By heating ammonium carbonate in sealed tubes to 130°.

Ninth.—By the slow evaporation of an aqueous solution of hydrocyanic acid.

Preparation.—Urea is obtained either from the urine, or synthetically from ammonium cyanate.

1. *From the urine.*—Fresh urine is evaporated to the consistency of a syrup over the water-bath; the residue is cooled and mixed with an equal volume of colorless nitric acid of sp. gr. 1.42; the crystals which separate are washed with a small quantity of cold water, and dissolved in hot water; the solution is decolorized, so far as possible, without boiling, with animal charcoal, filtered, and neutralized with potassium carbonate;

the liquid is then concentrated over the water-bath, and decanted from the crystals of potassium nitrate which separate; then evaporated to dryness over the water-bath, and the residue extracted with strong, hot alcohol; the alcoholic solution, on evaporation, leaves the urea more or less colored by urinary pigment.

2. *By synthesis.*—Urea is more readily obtained in a state of purity from potassium cyanate. This is dissolved in cold water, and dry ammonium sulphate is added to the solution. Potassium sulphate crystallizes out and is separated by decanting the liquid, which is then evaporated over the water-bath, fresh quantities of potassium sulphate crystallizing and being separated during the first part of the evaporation; the dry residue is extracted with strong, hot alcohol; this, on evaporation, leaves the urea, which, by a second crystallization from alcohol, is obtained pure.

Urea crystallizes from its aqueous solution in long, flattened prisms, and by spontaneous evaporation of its alcoholic solution in quadratic prisms with octahedral ends. It is colorless and odorless; has a cooling, bitterish taste, resembling that of saltpetre; is neutral in reaction; soluble in one part of water at 15°, the solution being attended with diminution of temperature; soluble in five parts of cold alcohol (sp. gr. 0.816) and in one part of boiling alcohol; very sparingly soluble in ether. When its powder is mixed with that of certain salts, such as sodium sulphate, the water of crystallization of the salt separates, and the mass becomes soft or even liquid. When pure it is not deliquescent, but is slightly hygrometric, and when it is to be weighed it should be dried at 100° and cooled in a dessicator.

Decompositions.—When heated to 130°, urea fuses; at a few degrees above that temperature it boils, giving off ammonia and ammonium carbonate, and leaves a residue of *ammelide*, $C_6H_9N_9O_9$. When heated to 150°—170°, it is decomposed, leaving a mixture of ammelide, cyanuric acid, and biuret:

$$\underset{\text{Urea.}}{8CON_2H_4} = \underset{\text{Carbon dioxide.}}{2CO_2} + \underset{\text{Ammelide.}}{C_6H_9N_9O_9} + \underset{\text{Ammonia.}}{7NH_3} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\text{Urea.}}{3CON_2H_4} = \underset{\text{Cyanuric acid.}}{C_3O_3N_3H_3} + \underset{\text{Ammonia.}}{3NH_3}$$

$$\underset{\text{Urea.}}{2CON_2H_4} = \underset{\text{Biuret.}}{C_2H_5N_3O_2} + \underset{\text{Ammonia.}}{NH_3}$$

One of the tests for urea is based upon the formation of biuret. If maintained at 150°—170° for some time, a dry, grayish mass remains, which consists principally of cyanuric acid. If, in this reaction, the volatile products be condensed, they will be found to contain urea, not that that substance is volatile, but because a portion of the cyanuric acid and ammonia have united to regenerate urea by the reverse action to that given above.

Dilute aqueous solutions of urea are not decomposed by boiling; but if the solution be concentrated, or the boiling prolonged for a long time, the urea is partially decomposed into carbon dioxide and ammonia. The same decomposition takes place more rapidly and completely when a solution of urea is heated under pressure to 140°.

A pure aqueous solution of urea is not altered by exposure to filtered air. If urine be allowed to stand, putrefactive changes take place under

the influence of a peculiar organized ferment, or of a diastase-like body which is a constituent of normal urine.

Chlorine decomposes urea with production of carbon dioxide, nitrogen, and hydrochloric acid. Solutions of the alkaline hypochlorites and hypobromites effect a similar decomposition in the presence of an excess of alkali, according to the equation:

$$\underset{\text{Urea.}}{CON_2H_4} + \underset{\substack{\text{Sodium}\\\text{hypochlorite.}}}{3ClONa} = \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen.}}{N_2} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{3ClNa}$$

Upon this decomposition are based the quantitative processes of Knop, Hüfner, Yvon, Davy, Leconte, etc.

Nitrous acid, or nitric acid charged with nitrous vapors, decomposes urea according to the equation:

$$\underset{\text{Urea.}}{CON_2H_4} + \underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{N_2O_3} = \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Nitrogen.}}{N_4} + \underset{\text{Water.}}{2H_2O} \quad (1)$$

or the equation:

$$\underset{\text{Urea.}}{2CON_2H_4} + \underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{N_2O_3} = \underset{\substack{\text{Ammonium}\\\text{carbonate.}}}{CO_3(NH_4)_2} + \underset{\text{Nitrogen.}}{N_4} + \underset{\substack{\text{Carbon.}\\\text{dioxide.}}}{CO_2} \quad (2)$$

If the mixture be made in the cold, of one molecule of nitrogen trioxide to two molecules of urea, the decomposition is that indicated by Equation 2. If, on the other hand, the trioxide be gradually added to the previously warmed urea solution in the same proportion, half the urea is decomposed while the remainder remains unaltered, and, upon the addition of a further and sufficient quantity of the trioxide, all the urea is decomposed according to Equation 1. Upon this reaction are based the processes of Gréhant, Boymond, Draper, etc.

When heated with mineral acids or alkalies, urea is decomposed with formation of carbon dioxide and ammonia; if the decomposing agent be an acid, carbon dioxide is given off, and an ammoniacal salt remains; if an alkali, a carbonate of the alkaline metal remains and carbon dioxide is given off. Upon this decomposition are based the processes of Heintz and Ragsky, Bunsen, etc.

Compounds.—Urea forms definite compounds, not only with acids, but also with certain oxides and salts. Of the compounds which it forms with *acids*, the most important are those with nitric and oxalic acids.

Urea nitrate, CON_2H_4,HNO_3, is formed as a white crystalline mass when a concentrated solution of urea is treated, in the cold, with nitric acid. It is much less soluble in water than is urea, especially in the presence of an excess of nitric acid. When heated to 140° it is decomposed with evolution of large quantities of carbon dioxide and nitrogen monoxide. It decomposes the carbonates with liberation of urea. If a solution of urea nitrate be evaporated over the water-bath, it is decomposed, bubbles of gas being given off beyond a certain degree of concentration, and large crystals of urea, covered with smaller ones of urea nitrate, separate. Zinc added to a solution of urea nitrate causes its decomposition with evolution of equal volumes of nitrogen and carbon dioxide.

Urea oxalate, $2CON_2H_4,H_2C_2O_4$—separates as a fine, crystalline powder from mixed aqueous solutions of urea and oxalic acid of sufficient concentration. It is acid in taste and reaction, less soluble in cold water than the nitrate, and less soluble in the presence of an excess of oxalic acid that in pure water. Its solution may be evaporated at the temperature of the water-bath without suffering decomposition.

Of the compounds of urea with *oxides*, the most interesting are those with mercuric oxide, three in number:

α. $CON_2H_4,2HgO$ is formed by gradually adding mercuric oxide to a solution of urea heated to near its boiling-point; the filtered liquid, on standing twenty-four hours, deposits crystalline crusts of the above composition.

β. $CON_2H_4,3HgO$ is formed as a gelatinous precipitate when mercuric chloride solution is added to a solution of urea containing potassium hydrate.

γ. $CON_2H_4,4HgO$ is formed as a white, amorphous precipitate when a dilute solution of mercuric nitrate is gradually added to a dilute alkaline solution of urea, and the excess of acid neutralized from time to time. A yellow tinge in the precipitate indicates the formation of mercuric subnitrate after the urea has been all precipitated (see Liebig's process, below).

Of the compounds of urea with *salts*, that with sodium chloride is the only one of importance:

$CON_2H_4,NaCl,H_2O$.—It is obtained in prismatic crystals when solutions of equal molecules of urea and sodium chloride are evaporated together. It is deliquescent and very soluble in water. Its solution, when mixed with solution of oxalic acid, only forms urea oxalate after long standing, or on evaporation.

Physiology.—Urea is a constant constituent of normal mammalian blood and urine, and is the chief product of the oxidation of albuminoid substances which occur in the body; the bulk of the nitrogen assimilated from the food ultimately making its exit from the body in the form of urea in the urine.

The determinations of the amount of urea in the blood and fluids other than the urine are, owing to imperfections in the processes of analysis, not as accurate as could be desired, the error being generally a minus one. As, however, the results of the same observer, using the same method, are comparable with each other, some of the more prominent are given in the following table:

QUANTITY OF UREA IN GRAMS PER 1,000 PARTS IN ANIMAL FLUIDS OTHER THAN URINE.

Normal blood—dog.....	0.36	Picard.
Normal blood—dog.....	0.19	Wurtz.
Normal blood—dog.....	0.11—0.58	Treskin.
Normal blood—dog.....	0.24—0.53	Munk.
Normal blood—dog.....	0.14—0.85	Pekelharing.
Normal blood—dog.....	0.22	Poiseuille & Gobley.
Normal blood—cow.....	0.22	Poiseuille & Gobley.
Normal blood—cow.....	0.19	Wurtz.
Normal blood—goat	0.17	Meissner & Shephard.

Normal blood—human	0.2 —0.4	Gamgee.
Normal blood—human	0.16	Picard.
Normal blood—human	0.14—0.18	Gautier.
Normal blood—human placental	0.28—0.62	Picard.
Normal blood—human fœtal	0.27	Picard.
Blood of dog before nephrotomy	0.26—0.88	Gréhant.
Blood of dog, three hours after nephrotomy	0.45—0.93	Gréhant.
Blood of dog, twenty-seven hours after nephrotomy	2.06—2.76	Gréhant.
Human blood in cholera	2.4	Voit.
Human blood in cholera	3.6	Chalvet.
Human blood in Bright's	15.0	Bright & Babington.
Lymph—dog	0.16	Wurtz.
Lymph—cow	0.19	Wurtz.
Chyle—cow	0.19	Wurtz.
Milk	0.13	Picard.
Saliva	0.35	Picard.
Bile	0.30	Picard.
Fluid of ascites	0.15	Picard.
Perspiration	0.43	Favre.
Perspiration	0.38	Funke.
Perspiration	0.88	Picard.

The quantity of urea contained in human urine under various circumstances of health and disease has been the subject of a great number of investigations, and a determination of the amount voided in a given case is frequently of great importance to the physician, as indicating the amount of disassimilation of nitrogenous material occurring in the body at the time. Under normal conditions the quantity of urea voided in twenty-four hours is subject to considerable variations, as is shown in the subjoined table:

AMOUNT OF UREA IN HUMAN URINE—NORMAL.

	Parts per 1,000.	Grams in total urine of 24 hours.	
Urine of sp. gr. 1009.2	9.88	.....	Millon.
Urine of sp. gr. 1011.6	11.39	.....	Millon.
Urine of sp. gr. 1019.0	18.58	.....	Boymond.
Urine of sp. gr. 1026.0	25.80	.....	Millon.
Urine of sp. gr. 1027.7	29.70	.....	Millon.
Urine of sp. gr. 1028.0	27.08	.....	Boymond.
Urine of sp. gr. 1029.0	31.77	.....	Millon.
Urine of adult male (average)	30.0	.....	Berzelius.
Urine of adult male (average)	....	28.052	Lecanu.
Urine of adult male (average)	25—32	22—35	Neubauer.
Urine of adult male (average)	....	32—43	Kerner.
Urine of adult male (average)	23 3	35	Vogel.
Urine of adult male, animal food	....	51—92	Franque.
Urine of adult male, mixed food	....	36—38	Franque.
Urine of adult male, vegetable food	....	24—28	Franque.
Urine of adult male, non-nitrogenized food	....	16	Franque.
Urine of old men 84—86 years	....	8.11	Lecanu.
Urine of adult female (average)	....	19:116	Lecanu.

AMOUNT OF UREA IN HUMAN URINE—NORMAL—*Continued.*

	Parts per 1,000.	Grams in total urine of 24 hours.	
Urine of pregnant female	....	30—38	Quinquand.
Urine of female, 24 hours after delivery	....	20—22	Quinquand.
Urine of infant, first day	....	0.03—0.04	Quinquand.
Urine of infant, fifth day	....	0.12—0.15	Quinquand.
Urine of infant, eighth day	....	0.2 —0.28	Quinquand.
Urine of infant, fifteenth day	....	0.3 —0.04	Quinquand.
Urine of child four years old	....	4.505	Lecanu.
Urine of child eight years old	....	13.471	Lecanu.
Urine of boy eighteen months old	....	8—12	Harley.
Urine of girl eighteen months old	....	6—9	Harley.

The variations are produced by:

First.—Age.—In new-born children the elimination of urea is insignificant. By growing children the amount voided is absolutely less than that discharged by adults, but, relatively to their weight, considerably greater; thus, Harley gives the following amounts of urea in grams for each pound of body-weight in twenty-four hours: boy, eighteen months, 0.4; girl, eighteen months, 0.35; man, twenty-seven years, 0.25; woman, twenty-seven years, 0.20. During adult life the mean elimination of urea remains stationary, unless modified by other causes than age. In old age the amount sinks to below the absolute quantity discharged by growing children.

Second.—Sex.—At all periods of life females eliminate less urea than males. The proportion given by Beigel differs slightly from that of Harley, viz.: one kilo of male, 0.35 grams urea in twenty-four hours; one kilo of female, 0.25 grams. During pregnancy females discharge more urea than males; very shortly after delivery the amount sinks to the normal, below which it passes during lactation.

Third.—Food.—The quantity of urea eliminated is in direct proportion to the amount of nitrogen contained in the food. The ingestion of large quantities of watery drinks increases the amount, and a contrary effect is produced by tea, coffee, and alcohol. With insufficient food the excretion of urea is diminished, although not arrested, even in extreme starvation.

Fourth.—Exercise.—The question whether the elimination of urea is increased during violent muscular exercise is one which has been the subject of many observations and of much discussion. An examination of the various results shows that, while the excretion of urea is slightly greater during violent exercise than during periods of rest, that increase is so insignificant in comparison to the work done, and, in some instances, to the loss of body-weight, as to render the assumption that muscular force is the result of the oxidation of the nitrogenized constituents of muscle improbable. (See Gamgee: Physiological Chemistry, i., pp. 385—401, for a full review of the subject.)

The percentage of urea in the urine of the same individual is not the same at different times of the day. The minimum hourly elimination is in the morning hours; an increase begins immediately after the principal meal, and reaches its height in about six hours, when a diminution sets in and progresses to the time of the next meal. Gorup-Besanez gives a curve representing the hourly variations in the elimination of urea, which, reduced to figures, gives the following:

Hour.	Urea in grams.	Hour.	Urea in grams.	Hour.	Urea in grams.
8–9 A.M.	1.5	4– 5 P.M.	2.6	12 1 A.M.....	1.9
9–10 A.M.....	1.5	5– 6 P.M.....	3.1	1–2 A.M.....	1.9
10–11 A.M.....	1.4	6– 7 P.M.....	2.8	2–3 A.M.....	1.9
11 A.M.–12 M...	1.3	7– 8 P.M.....	2 5	3–4 A.M.....	1.8
12 M.–1 P.M.....	1.8	8– 9 P.M.....	2.3	4–5 A.M.....	1.6
1–2 P.M.....	1.9	9–10 P.M.....	2.0	5–6 A.M.....	1.6
2–3 P.M.....	2.1	10–11 P.M.....	2.0	6–7 A.M.....	1.6
3–4 P.M.....	2.3	11–12 P.M.....	2.3	7–8 A.M.....	1.5

The total of which, however, represents a quantity above the normal.

The absolute amount of urea eliminated in twenty-four hours is increased by the exhibition of diuretics, alkalies, colchicum, turpentine, rhubarb, alkaline silicates, and compounds of antimony, arsenic, and phosphorus. It is diminished by digitalis, cafein, potassium iodide, and lead acetate; not sensibly affected by quinine.

Pathologically the quantity of urea voided may be either increased or diminished: an increase above the normal indicating an increased oxidation of nitrogenous material or the retention of the urea formed within the body; and a diminution a deficient oxidation of the same class of substances, or, as is frequently the case, a diminution in the supply of nitrogen to the body from loss of appetite or power of assimilation.

In acute febrile diseases both the relative and absolute amounts of urea eliminated augments, with some oscillations, until the fever is at its height; there is, however, no constant relation between the amount of urea eliminated and the body temperature. During the period of defervescence, the amount of urea eliminated in twenty-four hours is diminished below the normal; during convalescence it again slowly increases. If the malady terminate in death the diminution of urea is continuous to the end. In intermittent fever the amount of urea discharged is increased on the day of the fever and diminished during the interval. In cholera, during the algid stage, the elimination of urea by the kidneys is almost completely arrested, while the quantity in the blood is greatly increased. When the secretion of urine is again established, the excretion of urea is greatly increased (sixty to eighty grams a day), and the abundant perspiration is also rich in urea. In cardiac diseases, attended with respiratory difficulty, but without albuminuria, the elimination of urea is diminished and that of uric acid increased. In nephritis, attended with albuminuria, the elimination of urea at first remains normal; later it diminishes, and the urea, accumulating in the blood, gives rise to *uræmic poisoning*. The quantity of urea in the urine is also diminished in all diseases attended with dropsical effusions; it is increased when the dropsical fluid is reabsorbed. In true diabetes the amount of urea *in the urine of twenty-four hours* is greater than normal. In chronic diseases the elimination of urea is below the normal, owing to imperfect oxidation.

Tests for urea.—To detect the presence of urea in a fluid, it is mixed with three to four volumes of alcohol, and filtered after having stood several hours in the cold; the filtrate is evaporated on the water-bath, and the residue extracted with strong alcohol; the filtered alcoholic fluid is evaporated, and the residue tested as follows:

First.—A small portion is heated in a dry test-tube to about 160°,

until the odor of ammonia is no longer observed; the residue is treated with a few drops of caustic potassa solution and three or four drops of cupric sulphate solution. If urea be present, the biuret resulting from its decomposition by heat (p. 258) causes the solution of the cupric oxide with a reddish violet color.

Second.—A portion of the residue is dissolved in a drop or two of water and an equal quantity of *colorless* concentrated nitric acid added; if urea be present in sufficient quantity there appear white, shining, hexagonal or rhombic crystalline plates or six-sided prisms of urea nitrate.

Third.—A portion dissolved in water, as in second, is treated with a solution of oxalic acid; rhombic plates of urea oxalate crystallize.

Determination of quantity of urea in urine.—It must not be forgotten that, in all quantitative determinations of constituents of the urine, the question to be solved is not how much of that constituent is contained in a given quantity of urine, but how much of that substance the patient is discharging in a given time, usually twenty-four hours. Quantitative determinations are, therefor, in most cases, barren of useful results, unless the quantity of urine passed by the patient in twenty-four hours is known; and, in view of diurnal variations in elimination, unless the urine examined be a sample taken from the *mixed urine* of twenty-four hours.

There is no substance in the body for whose quantitative determination so many processes have been suggested; yet, although some of these are sufficiently accurate for clinical purposes, there has been none hitherto devised, which, as applied to the urine, is free from sources of error.

The processes giving the most accurate results are those of Bunsen and Draper, in both of which the urea is decomposed into carbon dioxide and ammonia, the former of which is weighed as barium carbonate. Unfortunately, both processes require an expenditure of time and a degree of skill in manipulation, which render their application possible only in a well-appointed laboratory.

A process which is described in all the text-books upon urinary analysis, and which is much used by physicians, is that of Liebig. As this method is one, however, which contains more sources of error than any other, and as it can only be made to yield approximately correct results by a very careful elimination, as far as possible, of those defects, it is not one which is adapted to the use of the physician.

Probably the most satisfactory process in the hands of the practitioner is that of Hüfner, based upon the reaction, to which attention was first called by Knop, of the alkaline hypobromites upon urea (p. 259); using, however, Dietrich's apparatus, or the more simple modification suggested by Rumpf, in place of that of Hüfner. The apparatus consists of a burette of 30—50 c.c. capacity, immersed in a reversed position in a glass cylinder, filled with water, and of such size that the burette can be completely immersed. The nozzle of the burette is connected with a piece of stout glass tubing about six inches long, bent at a right angle at about two inches from its upper end, and held by a support in such a way that the burette, which is to act as a gasometer, may be elevated or depressed at pleasure; the other end of the glass tubing is fitted to a piece of rubber tubing about three feet long. The other end of the rubber tube is connected with a short piece of glass tubing, which passes through an opening in a rubber cork, which has another hole giving passage to a short piece of glass tube fitted with a rubber tube closed with a pinch-cock; the rubber cork is inserted into the mouth of a wide-mouthed flask

of about 75 c.c. capacity; a short test-tube, of about 15 c.c. capacity, and of such size that it may be made to stand inside the bottle without spilling its contents; all joints must be air-tight.

The reagent required is made as follows: 27 c.c. of a solution of caustic soda, made by dissolving one hundred grams NaHO in 250 c.c. H_2O, are brought into a glass-stoppered bottle, 2.5 c.c. bromine are added, the mixture shaken, and diluted with water to 150 c.c. The caustic soda solution may be kept in a glass-stoppered bottle, whose stopper is well paraffined, but the mixture must be made up as required.

To conduct a determination, about 20 c.c. of the hypobromite solution are placed in the decomposing-bottle; 5 c.c. of the urine to be examined are placed in the test-tube, which is then introduced into the bottle, care being taken that no urine escapes, the cork is then inserted, the pinch-cock opened and the burette adjusted in the cylinder so that the level of the water cuts the highest point in the graduation. The pinch-cock is now closed and the decomposing bottle inclined and shaken, so that the urine and hypobromite solution mix; the decomposition begins at once, and the evolved nitrogen passes into the burette, which is raised from time to time, so as to keep the external and internal levels of water about equal; the carbon dioxide formed is retained by the soda solution. In about an hour (the decomposition is usually complete in fifteen minutes, but it is well to wait an hour) the height is so adjusted that the inner and outer levels of water are exactly even and the graduation is read, while the standing of the barometer and thermometer are noted at the same time.

In calculating the percentage of urea from the volume of nitrogen obtained, it is essential that a correction should be made for differences of temperature and pressure, without which the result from an ordinary sample of urine may be vitiated by an error of ten per cent. If, however, the temperature and barometric pressure have been noted, the correction is readily made by the use of the table on pages 266 and 267, computed by Dietrich.

In the square of the table in which the horizontal line of the observed temperature crosses the vertical one of the observed barometric pressure will be found the correct weight, in milligrams, of a cubic centimetre of nitrogen; this, multiplied by the observed volume of nitrogen, gives the weight of nitrogen furnished by the urea. But as 60 parts of urea yield 28 of nitrogen, the weight of nitrogen multiplied by 2.14 gives the weight of urea in milligrams contained in the 5 c.c. (or other quantity) of urine decomposed. This quantity, multiplied by twice the amount of urine passed in 24 hours, and divided by 1,000, gives the amount of urea eliminated in 24 hours in grams.

Example.—5 c.c. of urine decomposed; barometer = 742; thermometer=20; nitrogen collected=14.5.

From the table, the weight of 1 c.c. N at the above temperature and pressure is 1.116. $1.116 \times 14.5 = 16.18$ milligr. nitrogen collected; $16.18 \times 2.14 = 34.625$ milligr. urea in 6 c.c. urine. The patient passed in 24 hours 650 c.c. urine, $\frac{1300 \times 34.63}{1,000} = 45.02$ grams urea passed in 24 hours.

In using this process it is well to have the urea solution as near the strength of one per cent. as possible; therefor, if the urine be concentrated, as in the above example, it should be diluted. Even when carefully conducted, the process is not strictly accurate; creatinin and uric acid are also decomposed with liberation of nitrogen, thus causing a slight plus

TABLE OF THE WEIGHT OF ONE

Temperature in Centigrade.	720	722	724	726	728	730	732	734	736	738	740	742	744
10°	1.1388	1.1370	1.1402	1.1434	1.1466	1.1498	1.1529	1.1561	1.1593	1.1625	1.1657	1.1689	1.1721
11°	1.1288	1.1320	1.1352	1.1384	1.1415	1.1447	1 1479	1.1511	1.1543	1.1574	1.1606	1.1638	1.1670
12°	1.1287	1.1269	1.1301	1.1333	1.1364	1.1396	1.1428	1.1459	1.1491	1.1523	1 1554	1.1586	1.1618
13°	1.1187	1.1219	1.1251	1.1282	1.1314	1.1345	1.1377	1.1409	1.1440	1.1472	1.1503	1.1535	1.1566
14°	1.1136	1.1168	1.1200	1.1231	1.1263	1.1294	1.1326	1.1357	1.1389	1.1420	1.1452	1.1483	1.1515
15°	1.1085	1.1117	1.1149	1.1180	1.1211	1.1243	1.1274	1.1305	1.1337	1.1368	1.1399	1.1431	1.1462
16°	1.1034	1.1066	1.1097	1.1128	1.1160	1.1191	1.1222	1.1253	1.1285	1.1316	1.1347	1.1378	1.1409
17°	1.0983	1.1014	1.1045	1.1076	1.1107	1.1138	1.1170	1 1201	1.1232	1.1263	1.1294	1.1325	1.1356
18°	1.0930	1.0961	1.0992	1.1023	1.1054	1.1085	1.1117	1.1148	1.1179	1.1209	1.1241	1.1272	1.1303
19°	1.0877	1.0908	1.0939	1.0970	1.1001	1.1032	1.1063	1.1094	1.1125	1.1156	1.1187	1.1218	1.1248
20°	1.0825	1.0855	1.0886	1.0917	1.0948	1.0979	1.1009	1.1040	1.1071	1.1102	1.1133	1.1164	1.1194
21°	1.0771	1.0802	1.0832	1.0863	1.0894	1.0924	1.0955	1.0986	1.1017	1.1047	1.1078	1.1109	1.1139
22°	1.0717	1.0747	1.0778	1.0808	1.0839	1.0870	1.0900	1.0931	1.0961	1.0992	1.1023	1.1053	1.1084
23°	1.0662	1.0692	1.0723	1.0753	1.0784	1.0814	1.0845	1.0875	1.0906	1.0936	1.0967	1.0997	1.1028
24°	1.0606	1.0636	1.0667	1.0697	1.0728	1.0758	1.0789	1.0819	1.0849	1.0880	1.0910	1.0940	1.0971
25°	1.0550	1.0580	1.0610	1.0641	1.0671	1.0701	1.0732	1.0762	1.0792	1.0823	1.0853	1.0883	1.0913
	720	722	724	726	728	730	732	734	736	738	740	742	744

Barometric pressure in millimetres.

error; on the other hand, a minus error is caused by the fact, that in the decomposition of urea by the hypobromite, the theoretical result is never obtained within about eight per cent. in urine. These errors may be rectified to a great extent by multiplying the result by 1.044.

A process which does not yield as accurate results as the preceding, but which is much more easy of application, is that of Fowler, based upon the loss of specific gravity of the urine after the decomposition of its urea by hypochlorite. To apply this method the specific gravity of the urine is carefully determined, as well as that of the liq. sodæ chlorinatæ (Squibb's). One volume of the urine is then mixed with exactly seven volumes of the liq. sod. chlor., and, after the first violence of the reaction has subsided, the mixture is shaken from time to time during an hour, when the decomposition is complete; the specific gravity of the mixture is then determined. As the reaction begins instantaneously when the urine and reagent are mixed, the specific gravity of the mixture must be calculated by adding together once the specific gravity of the urine and seven times the specific gravity of the liq. sod. chlor., and dividing the sum by eight. From the quotient so obtained the specific gravity of the mixture after decomposition is subtracted; every degree of loss in specific gravity indicates 0.7791 gram of urea in 100 c.c. of urine. The specific gravity determinations must all be made at the same temperature; and that of the mixture only when the evolution of gas has ceased entirely.

Finally, when it is only desired to determine whether the urea is greatly in excess or much below the normal, advantage may be taken of the formation of crystals of urea nitrate. Two samples of the urine are taken, one of 5 c.c. and one of 10 c.c.; the latter is evaporated, at a low temperature, to the bulk of the former and cooled; to both one-third volume of colorless nitric acid is added. If crystals do not form within a few moments in the concentrated sample, the quantity of urea is below the normal; if they do in the unconcentrated sample, it is in excess. In using this very rough method, regard must be had to the quantity of

CUBIC CENTIMETRE OF NITROGEN.

746	748	750	752	754	756	758	760	762	764	766	768	770	
1.1753	1.1785	1.1817	1.1848	1.1880	1.1912	1.1944	1.1976	1.2008	1.2040	1.2072	1.2104	1.2136	10°
1.1701	1.1733	1.1765	1.1717	1.1829	1.1860	1.1892	1.1924	1.1956	1.1988	1 2019	1.2051	1.2083	11°
1.1649	1.1681	1.1713	1.1744	1.1776	1.1808	1.1839	1.1871	1.1903	1.1934	1.1966	1.1998	1.2029	12°
1.1598	1.1630	1.1661	1.1693	1.1724	1.1756	1.1787	1.1819	1.1851	1.1882	1.1914	1.1945	1.1977	13°
1.1546	1.1577	1.1609	1.1640	1.1672	1.1703	1.1735	1.1766	1.1798	1.1829	1.1861	1.1892	1.1923	14°
1.1498	1.1525	1.1556	1.1587	1.1619	1.1650	1.1681	1.1713	1.1744	1.1775	1.1807	1.1838	1.1869	15°
1.1441	1.1472	1.1503	1.1534	1.1566	1.1597	1.1628	1.1659	1.1691	1.1722	1.1753	1.1784	1.1816	16°
1 1397	1.1419	1.1450	1.1481	1.1512	1.1543	1.1574	1.1605	1.1636	1.1667	1.1699	1.1730	1.1761	17°
1.1334	1.1365	1.1396	1.1427	1.1458	1.1489	1.1520	1.1551	1.1582	1.1613	1.1644	1.1675	1.1706	18°
1.1279	1.1310	1.1341	1.1372	1.1403	1.1434	1.1465	1.1496	1.1527	1.1558	1.1589	1.1620	1.1650	19°
1.1225	1.12 6	1.1287	1.1318	1.1348	1.1379	1.1410	1.1441	1.1472	1.1502	1.1533	1.1564	1.1595	20°
1.1170	1.1201	1.1231	1.1262	1.1293	1.1324	1.1354	1.1385	1.1416	1.1446	1.1477	1.1508	1.1539	21°
1.1115	1.1145	1.1176	1.1206	1.1237	1.1268	1.1298	1.1329	1.1359	1.1390	1.1421	1.1451	1.1482	22°
1.1058	1.1089	1.1119	1.1150	1.1180	1.1211	1.1241	1.1272	1.1302	1.1333	1.1363	1.1394	1.1424	23°
1.1001	1.1032	1.1062	1.1092	1.1123	1.1153	1.1184	1.1214	1.1244	1.1275	1.1305	1.1336	1.1366	24°
1.0944	1.0974	1.1004	1.1035	1.1065	1.1095	1.1126	1.1156	1.1186	1.1216	1.1247	1.1277	1.1307	25°
746	748	750	752	754	756	758	760	762	764	766	768	770	

Temperature in Centigrade.

Barometric pressure in millimetres.

urine passed in twenty-four hours; the above applies to the normal amount of 1,200 c.c.; if the quantity be greater or less, the urine must be concentrated or diluted in proportion.

Obviously this process cannot be used when the urine is albuminous.

Sulphurea, $CS\langle^{NH_2}_{NH_2}$,

is a compound bearing the same relation to urea that carbon disulphide bears to carbon dioxide, and may be obtained from ammonium sulphocyanate as urea is obtained from ammonium cyanate. It forms large prismatic crystals or long needles, very soluble in water and alcohol, difficultly soluble in ether. It forms salts and other compounds, similar to those of urea in constitution.

Compound Ureas.

These compounds, which are exceedingly numerous, may be considered as formed by the substitution of one or more alcoholic or acid radicals for one or more of the remaining hydrogen atoms of urea.

Those containing alcoholic radicals may be obtained, as urea is obtained from ammonium cyanate, from the cyanate of the corresponding compound ammonium; or by the action of ammonia, or of the compound ammonias, upon the cyanic ethers.

Those containing acid radicals have received the distinctive name of *ureids;* some of them are of great interest as derivatives of uric acid, which is itself probably an ureid. We will limit our consideration of these bodies to uric acid and the ureids obtained from and related to it.

Uric Acid—Lithic Acid—$C_5H_4N_4O_3$.

Constitution unknown. So far as yet known, uric acid is exclusively an animal product. It exists in the urine of man and of the carnivora, and in that of the herbivora when, during early life or starvation, they are for the time being carnivora; as a constituent of urinary calculi; and very abundantly in the excrement of serpents, tortoises, birds, molluscs, and insects, also in guano. It is present in very small quantity in the blood of man, more abundantly in that of gouty patients and in that of birds; the so-called "chalk-stones" deposited in the joints of gouty patients are composed of sodium urate. It also occurs in the spleen, lungs, liver, pancreas, brain, and muscular fluid.

Although uric acid may be obtained from calculi, urine, and guano, the source from which it is most readily obtained in a state of purity is the solid urine of large serpents, which is composed almost entirely of uric acid and the acid urates of sodium, potassium, and ammonium. This is dried, powdered, and dissolved in a solution of potassium hydrate, containing one part of potash to twenty of water; the solution is boiled until all odor of ammonia has disappeared. Through the filtered solution a current of carbon dioxide is passed, through a wide tube, until the precipitate, which was at first gelatinous, has became granular and sinks to the bottom; the acid potassium urate so formed is collected on a filter, and washed with cold water until the wash-water becomes turbid when added to the first filtrate; the deposit is now dissolved in hot dilute caustic potassa solution, and the solution filtered hot into hydrochloric acid diluted with an equal volume of water. The precipitated uric acid is washed and dried.

Uric acid, when pure, crystallizes in small, white, rhombic, rectangular or hexagonal plates, or in rectangular prisms, or in dendritic crystals of a hydrate, $C_5H_4N_4O_3,2H_2O$. As crystallized from urine it is more or less colored with urinary pigments, and forms rectangular or rhombic plates, usually with the angles rounded so as to form lozenges, which are arranged in bundles, daggers, crosses, or dendritic groups, sometimes of considerable size. It is almost insoluble in water, requiring for its solution nineteen hundred parts of boiling water and fifteen thousand parts of cold water; insoluble in alcohol and ether; its aqueous solution is acid to test-paper; cold hydrochloric acid dissolves it more readily than water, and on evaporation deposits it in rectangular plates. It is tasteless and odorless.

When heated, uric acid neither fuses nor sublimes, but is decomposed with formation of hydrocyanic and cyanuric acids, urea and ammonium cyanate. When heated in a current of chlorine, it yields cyanuric and hydrochloric acids; when a current of chlorine is passed for some time through water holding uric acid in suspension, alloxan, parabanic and oxalic acids, and ammonium cyanate are formed; similar decompositions are produced by bromine and iodine. Hydrochloric acid simply dissolves it. Sulphuric acid dissolves it; a hot solution deposits a deliquescent crystalline compound, $C_5H_4N_4O_3,4SO_4H_2$; when heated with sulphuric acid to 140° for some time, it is partly decomposed with formation of *hydurilic acid* and *pseudoxanthine*. Ozone oxidizes uric acid with formation of allantoin, carbon dioxide, and urea. The action of nitric acid varies with the temperature; it dissolves in cold nitric acid with effervescence and formation of alloxan, alloxantine, and urea, which last is

itself decomposed by the excess of nitric acid. On heating the mixture, or by oxidation of uric acid with hot nitric acid, the alloxan and alloxantine formed are converted into parabanic acid. A solution of uric acid in nitric acid, treated with ammonium hydrate and slightly heated, turns purple from the formation of *murexid* or *ammonium purpurate* (see p. 270). Solutions of the alkalies dissolve uric acid with formation of neutral urates. Uric acid is bibasic, forming two series of salts with the alkaline metals.

It is more convenient to consider the urates in this place than under their respective metallic elements.

Ammonium urates.—The neutral salt, $C_5H_2N_4O_3(NH_4)_2$, is unknown. The acid salt, $C_5H_3N_4O_3(NH_4)$, exists as a constituent of the urine of the lower animals, and occurs, accompanying other urates and free uric acid, in urinary sediments and calculi. Sediments of this salt are rust-yellow or pink in color, amorphous, or composed of globular masses, set with projecting points, or elongated dumb-bells, and are formed in alkaline urine. It is very sparingly soluble in water; soluble in warm hydrochloric acid, from which solution crystalline plates of uric acid are deposited.

Potassium urates.—The neutral salt, $C_5H_2N_4O_3K_2$, is obtained when a solution of potassium hydrate, free from carbonate, is saturated with uric acid; the solution on concentration deposits the salt in fine needles. It is soluble in forty-four parts of cold water and in thirty-five parts of boiling water. It is alkaline in taste, and absorbs carbon dioxide from the air.

The acid salt, $C_5H_3N_4O_3K$, is formed as a granular (at first gelatinous) precipitate when a solution of the neutral salt is treated with carbon dioxide. It dissolves in eight hundred parts of cold water and in eighty parts of boiling water. The occurrence of potassium urates in urinary sediments and calculi is very exceptional.

Sodium urates.—The neutral salt, $C_5H_2N_4O_3Na_2$, is formed under similar conditions as the corresponding potassium salt. It forms nodular masses, soluble in seventy-seven parts of cold water and in seventy-five of boiling water; it absorbs carbon dioxide from the air.

The acid salt, $C_5H_3N_4O_3Na$, is formed when the neutral salt is treated with carbon dioxide. It is soluble in twelve hundred parts of cold water and in one hundred and twenty-five parts of boiling water. It occurs in urinary sediments and calculi, very rarely crystallized. The arthritic calculi of gouty patients are almost exclusively composed of this salt, frequently beautifully crystallized.

Calcium urates.—The neutral salt, $C_5H_2N_4O_3Ca$, is obtained by dropping a solution of neutral potassium urate into a boiling solution of calcium chloride until the precipitate is no longer redissolved, and then boiling for an hour. A granular powder, soluble in fifteen hundred parts of cold water and in fourteen hundred and forty parts of boiling water.

The acid salt, $(C_5H_3N_4O_3)_2Ca$, is obtained by decomposing a boiling solution of acid potassium urate with calcium chloride solution. It crystallizes in needles, soluble in six hundred and three parts of cold water and in two hundred and seventy-six parts of boiling water. It occurs occasionally in urinary sediments and calculi, and in "chalk stones."

Lithium urates.—The acid salt, $C_5H_3N_4O_3Li$, is formed by dissolving uric acid in a warm solution of lithium carbonate. It crystallizes in needles, which dissolve in sixty parts of water at 50°, and do not separate

when the solution is cooled. It is with a view to the formation of this, the most soluble of the urates, that the compounds of lithium are given to patients suffering with the uric acid diathesis.

Physiology.—Uric acid exists in the economy chiefly in combination as its sodium salts; it is occasionally found free, and from the probable method of its formation it is difficult to understand how all the uric acid in the economy should not have existed there free, at least at the instant of its formation. It can scarcely be doubted, although there is no experimental proof in support of this view, that uric acid is one of the products of the oxidation of the albuminoid substances—an oxidation intermediate in the production of urea; and that consequently diseases in which there is an excessive formation of uric acid, such as gout, have their origin in defective oxidation.

In human urine the quantity of uric acid varies with the nature of the food in the same manner as does urea, and about in the same proportion:

	Urea.	Uric acid.	Proportion of uric acid to urea.
Animal food.....	71.5	1.25	57.2
Mixed food.....	37.0	0.76	48.7
Vegetable food	26.0	0.50	52.0
Non-nitrogenized food.....	16.0	0.34	47.0

The mean elimination of uric acid in the urine is from one-thirty-fifth to one-sixtieth of that of urea, or about 0.5 to 1.0 gram in twenty-four hours. With a strictly vegetable diet the elimination in 24 hours may fall to 0.3 grams, and with a surfeit of animal food it may rise to 1.5 grams. The hourly elimination is increased after meals, and diminished by fasting and by muscular and mental activity.

Deposits of free uric acid occur in acid, concentrated urines. In gout the proportion of uric acid in the urine is diminished, although, owing to the small quantity of urine passed, it may be relatively great; during the paroxysms the quantity of uric acid is increased both relatively and absolutely. The proportion of uric acid in the blood is invariably increased in gout.

Tests.—Uric acid may be recognized by its crystalline form and by the *murexid test.* To apply this test the substance is moistened with nitric acid, which is evaporated nearly to dryness at a low temperature; the cooled residue is then moistened with ammonium hydrate. If uric acid be present, a yellow residue—sometimes pink or red when the uric acid was abundant—remains after the evaporation of the nitric acid, and this, on the addition of the alkali, assumes a rich purplish red color.

To detect uric acid in the blood, about two drachms of the serum are placed in a flat glass dish and faintly acidulated with acetic acid; a very fine fibril of linen thread is placed in the liquid, which is set aside and allowed to evaporate to the consistency of a jelly; the fibril is then removed and examined microscopically. If the blood contain uric acid in abnormal proportion, the thread will have attached to it crystals of uric acid.

Quantitative determination.—The best method for the determination of the quantity of uric acid in urine is the following: 250 c.c. of the filtered urine are acidulated with 10 c.c. of hydrochloric acid, and the mixture set aside for twenty-fours in a cool place. A small filter is washed, first with dilute hydrochloric acid and then with water, dried at 100°, and weighed. At the end of the twenty-four hours this filter is moistened in

a funnel, and the crystals of uric acid collected upon it (those which adhere to the walls of the precipitating vessel are best separated by a small section of rubber tubing passed over the end of a glass rod, and used as a brush). No water is to be used in this part of the process, the filtered urine being passed through a second time, if this be required, to bring all the crystals upon the filter. The deposit on the filter is now washed with 35 c.c. of pure water, added in small portions at a time; the filter and its contents are then dried and weighed. The difference between this weight and that of the filter alone is the weight of uric acid in 250 c.c. of urine. If from any cause more than 35 c.c. of wash-water have been used, $0^{mgr.}$. 043 must be added to this weight for every c.c. of extra wash-water.

If the urine contain albumen, this must first be separated by adding two or three drops of acetic acid, heating to near 100°, until the coagulum becomes flocculent, and filtering.

Ureids derived from Uric Acid.

These substances are quite numerous, and are divisible into ureids, diureids, triureids, and uramic acids, according as they are formed by substitution in one, two, or three molecules of urea, and according as the acid radical substituted does or does not retain a group COOH. The more prominent may be arranged in two parallel groups, the corresponding terms of which differ from each other by CO, thus :

UREIDS.

Parabanic series.

$C_3H_2N_2O_3$	$C_3H_4N_2O_3$	$C_3H_4N_2O_2$
Oxalylurea (parabanic acid).	Glyoxylurea (allanturic acid).	Glycolylurea (hydantoin).

Alloxanic series.

$C_4H_2N_2O_4$	$C_4H_4N_2O_4$	$C_4H_4N_2O_3$
Mesoxalylurea (alloxan).	Tartryonylurea (dialyuric acid).	Malonylurea (barbituric acid).

DIUREIDS.

$C_4H_6N_4O_3$	$C_6H_4N_4O_5$	$C_5H_6N_4O_4$	$C_8H_4N_4O_7$
Glyoxyldiurea (allantoin).	Oxalyl-glyoxyldiurea (oxalantine).	Tartronyldiurea (pseudo-uric acid).	Mesoxalyl-tartronyldiurea (alloxantine).

URAMIC ACIDS.

$C_3H_6N_2O_3$	$C_3H_4N_2O_4$	$C_4H_4N_2O_5$
Hydantoic acid.	Oxaluric acid.	Alloxanic acid.

Some of these substances require a brief mention :

Oxalylurea, or *parabanic acid*, is urea in which two atoms of hydrogen have been replaced by the divalent radical $(C_2O_2)''$ of oxalic acid. It is obtained by the oxidation of uric acid, or of alloxan by hot nitric acid. It forms six-sided transparent prisms, acid in taste, and very soluble in water and alcohol.

Glyoxyldiurea, or *allantoin*, is, as its more common name implies, obtained from the allantoic fluid of the cow; it has also been found to exist in the urine of sucking calves, in that of dogs and cats when fed upon meat, in that of children during the first eight days of life, in that of adults after the ingestion of tannin, and in that of pregnant women.

It may be obtained artificially by oxidizing uric acid held in suspension in boiling water, with pure oxide of lead.

It crystallizes in small, odorless, tasteless, colorless, neutral and transparent prisms; sparingly soluble in cold water, readily in warm water, alcohol, and ether. When heated with alkalies it yields oxalic acid and ammonia; with dilute acids, *allanturic acid;* and with oxidizing agents, urea and *allantoic acid.*

It is probably, like uric acid, an intermediate product of the oxidation of the albuminoids.

Mesoxalylurea, or *alloxan*, is a product of the limited oxidation of uric acid. It has been found in one instance in the intestinal mucus, in a case of diarrhœa, and probably in the urine in a case of heart disease.

It forms colorless crystals, readily soluble in water. When exposed to the air it gradually turns red, which color it communicates to the skin on contact with it.

Oxaluric acid occurs, as its ammonium salt, as a normal constituent, in small but constant quantity, of human urine, from which it can only be obtained by operating upon large quantities. It may also be obtained by heating parabanic acid with calcium carbonate.

It forms a white, sparingly soluble powder, which, on boiling with water or with the alkalies, is converted into urea and oxalic acid. The ammonium salt crystallizes in white, glistening needles, sparingly soluble in water.

Its ready conversion into urea and oxalic acid, and its formation from parabanic acid, itself a product of oxidation of uric acid, shows it to be one of the numerous terms in the oxidation of the nitrogenous constituents of the body.

Substances of Unknown Constitution Related to Uric Acid.

There exist several substances, of unknown constitution, which, from their products of decomposition and their occurrence, seem to be closely related to uric acid; some of these occur in the animal economy: xanthine, hypoxanthine, guanine, carnine.

Xanthine, $C_5H_4N_4O_2$.

Sometimes called *xanthic oxide* or *urous acid*, was first discovered as a constituent of a rare form of urinary calculus; since that time it has been found to exist in small quantity in the pancreas, spleen, liver, thymus and brain of mammals and fishes; also in human urine after the use of sulphur baths and inunctions.

When dry it forms an amorphous, yellowish white powder; very sparingly soluble in cold water, rather more freely in hot water. If dissolved in nitric acid and the solution evaporated by heat, xanthine leaves a yellow residue, which assumes a reddish yellow color on contact with potassium hydrate solution, and this when heated turns violet-red.

Xanthine calculi are of very infrequent occurrence; they vary in size from that of a pea to that of a pigeon's egg; are rather hard, brownish yellow, smooth, shining, and made up of well-defined, concentric layers; their broken surface assumes a waxy polish when rubbed.

Hypoxanthine—Sarcine—$C_5H_4N_4O$,

was discovered in the spleen; it has also been found to exist in the muscular tissue of mammals, in the thymus, suprarenal capsules, and brain; in the human liver in acute yellow atrophy; and in the blood and urine, accompanied by xanthine, in leucocythæmia; and probaby in small quantity in healthy blood; and in the marrow of bones.

It is best obtained from the mother-liquor of the preparation of creatine (*q. v.*); this is diluted with water, rendered alkaline with ammonium hydrate, and treated with silver nitrate in ammonical solution; the precipitate is washed with dilute ammonia by decantation, collected on a filter, and extracted with boiling nitric acid; sp. gr. 1.1; the nitric acid solution, on cooling, deposits a compound of silver nitrate and hypoxanthine; this is suspended in water, decomposed by hydrogen sulphide; the filtered solution on concentration deposits crystals of hypoxanthine nitrate.

Free hypoxanthine, obtained from the nitrate by decomposition with ammonium hydrate, forms nodular masses, never crystals; soluble in three hundred parts cold and seventy-eight parts boiling water, sparingly soluble in alcohol, readily in dilute acids and alkalies, with which and with metallic salts it forms compounds. It may be obtained from uric acid or xanthine by the action of sodium amalgam, and when oxidized with nitric acid it yields xanthine. The close relationship of these bodies is shown by the formulæ:

Uric acid	$C_5H_4N_4O_3$
Xanthine	$C_5H_4N_4O_2$
Hypoxanthine	$C_5H_4N_4O$

The flesh of the ox contains 0.022 per cent. of hypoxanthine; that of the rabbit 0.026 per cent.; leucocythæmic blood 0.0075 per cent.

Guanine, $C_5H_5N_5O$,

as its name implies, was first obtained from guano; it has also been found in the pancreas, lungs and liver of certain mammalians, and in the excrements of the lower orders.

It appears as a white or yellowish amorphous mass; odorless and tasteless; almost insoluble in water, alcohol and ether; readily in acids and alkalies, with which it forms compounds.

Carnine, $C_7H_8N_4O_3 + H_2O$,

has been obtained from Liebig's meat extract. It forms chalky, microscopic crystals; sparingly soluble in cold, readily in warm water; insoluble in alcohol and ether. Forms compounds with acids and alkalies similar to those of hypoxanthine.

Carbamic Acid, $\begin{matrix}COOH\\|\\NH_2\end{matrix}$,

has not been isolated, and is only known in combination as its ammonium salt and in its ethers; the latter are known under the generic name of *urethanes*. Its ammonium salt exists in sesquicarbonate of ammonium (*q. v.*), and has been said to exist in blood-serum (see p. 256).

The remaining acids of this series, being monobasic, each forms a single amide. None of these amides are of other than theoretic interest.

Amides of the Acid Series, $C_nH_{2n-2}O_4$.

Oxamide, $\begin{matrix}CO-NH_2\\|\\CO-NH_2\end{matrix}$, was one of the first of this class of substances obtained. It is formed by depriving ammonium oxalate of the elements of two molecules of water, or by the action of ammonia upon ethyl oxalate.

It forms a light, white, crystalline powder; odorless, tasteless, and neutral; almost insoluble in cold water, sparingly soluble in warm water. It is decomposed by sulphuric acid into the two oxides of carbon and ammonium sulphate; by phosphoric anhydride into water and cyanogen; by mercuric oxide into urea and carbon dioxide; and by acids and alkalies into oxalic acid and ammonia.

Corresponding to it there exist a number of substances constituted by the substitution of alcoholic radicals for the remaining hydrogen atoms, and consequently comparable to the ureids.

Oxamic acid, $\begin{matrix}CO-NH_2\\|\\CO,OH\end{matrix}$, is formed by the dry distillation of ammonium oxalate at 220°—230°. It appears as a fine, colorless powder; sparingly soluble in water and alcohol; insoluble in ether; fusible at 173°.

The remaining acids of this series are capable of forming compounds similar to the above, none of which, however, require further notice.

TRIATOMIC ALCOHOLS.

There is as yet only one alcohol known containing a trivalent radical. This is *glycerin*, whose relation to the monoatomic and diatomic alcohols is shown by the following formulæ:

Propane.	Propyl alcohol.	Propyl glycol.	Glycerin.
CH_3	CH_3	CH_2OH	CH_2OH
$\vert$	$\vert$	$\vert$	$\vert$
CH_2	CH_2	CH_2	$CHOH$
$\vert$	$\vert$	$\vert$	$\vert$
CH_3	CH_2OH	CH_2OH	CH_2OH

Glycerin, $CH_2(OH)_2$,

was first obtained as a secondary product in the manufacture of lead plaster; it is now produced as a by-product in the manufacture of soaps and of stearin candles. It exists free in palm-oil and in other vegetable oils; it is produced in small quantity during alcoholic fermentation, and is consequently present in wine and beer. It is much more widely disseminated in its ethers, the neutral fats, in the animal and vegetable kingdoms.

It has been obtained by partial synthesis, by heating for some time a mixture of allyl tribromide, silver acetate and acetic acid, and saponifying the triacetin so obtained.

The glycerin obtained by the process now generally followed—the decomposition of the neutral fats and distillation of the products in a current of superheated steam—is free from the impurities which contaminated the products of the older processes. The only impurity likely to be present is water, which may be recognized by the low specific gravity of the mixture.

Glycerin is a colorless, odorless, syrupy liquid; has a sweetish taste; sp. gr. 1.26 at 15°. Although it cannot usually be caused to crystallize by the application of the most intense cold, it does so sometimes under imperfectly understood conditions, forming small white needles of sp. gr. 1.268, and fusible between 7° and 8°; it is soluble in all proportions in water and alcohol, insoluble in ether and in chloroform. The specific gravity of mixtures of glycerin and water are:

Per cent. glycerin.	Specific gravity.	Per cent. glycerin.	Specific gravity.	Per cent. glycerin.	Specific gravity.
10	1.024	40	1.105	70	1.170
20	1.051	50	1.127	80	1.220
30	1.075	60	1.159	90	1.232

Glycerin is a solvent of a great number of mineral and organic substances; 100 parts of glycerin dissolve:

	Parts.		Parts.		Parts.
Sodium carbonate	98.0	Ammonium chloride	20.0	Strychnine nitrate	3.85
Borax	60.0	Sodium chloride	20.0	Potassium chlorate	3.5
Tannin	50.0	Arsenious acid	20.0	Atropine	3.0
Urea	50.0	Arsenic acid	20.0	Quinine sulphate	2.75
Potassium arsenate	50.0	Ammonium carbonate	20.0	Brucine	2.25
Sodium arsenate	50.0	Lead acetate	20.0	Iodine	1.9
Zinc chloride	50.0	Morphine chloride	20.0	Veratrine	1.0
Potassium iodide	40.0	Ferric lactate	16.0	Quinine tannate	0.77
Zinc iodide	40.0	Oxalic acid	15.0	Quinine	0.5
Alum	40.0	Barium chloride	10.0	Cinchonine	0.5
Zinc sulphate	35.0	Boric acid	10.0	Morphine	0.45
Atropine sulphate	33.0	Benzoic acid	10.0	Mercuric iodide	0.29
Potassium cyanide	32.0	Calcic sulphide	10.0	Strychnine	0.25
Cupric sulphate	30.0	Potassium sulphide	10.0	Phosphorus	0.20
Mercuric cyanide	27.0	Sodium bicarbonate	8.0	Sulphur	0.10
Potassium bromide	25.0	Mercuric chloride	7.5	Sugar	40.0
Ferrous sulphate	25.0	Cinchonine sulphate	6.7	Gum	28.5
Strychnine sulphate	22.5	Tartar emetic	5.5		

The following substances are soluble in glycerin in all proportions:

Bromine.	Nitric acid.	Ammonia.
Ferrous iodide.	Hydrochloric acid.	Potassium hydrate.
Antimony trichloride.	Phosphoric acid.	Sodium hydrate.
Ferric chloride.	Acetic acid.	Codeine.
Sodium hypochlorite.	Tartaric acid.	Silver nitrate.
Potassium hypochlorite.	Citric acid.	Mercurous nitrate.
Sulphuric acid.	Lactic acid.	

When glycerin is heated, a portion distils unaltered between 275°—280°; the greater part, however, is decomposed, giving off acrolein, acetic acid, carbon dioxide, and combustible gases. It may be distilled without decomposition in a current of superheated steam, the temperature being maintained between 288°—315°.

Platinum black oxidizes glycerin with the production, finally, of water and carbon dioxide; oxidized by manganese dioxide and sulphuric acid, it yields carbon dioxide and formic acid. The action of nitric acid on glycerin varies with the conditions; if a layer of glycerin, diluted with water, is floated on nitric acid of sp. gr. 1.5, glyceric acid is formed; by the action of a mixture of concentrated nitric and sulphuric acids on glycerin, nitro-glycerin (*q. v.*) is formed.

When heated with an alkaline hydrate, it forms a mixture of potassium formiate and acetate. Phosphoric anhydride removes from it the elements of water, to form acrolein (*q. v.*); the same change is produced when glycerin is heated with sulphuric acid or with potassium hydrosulphate. When heated with oxalic acid, it is decomposed into carbon dioxide and formic acid.

Uses.—Glycerin is very extensively used in the arts and in medicine. Being unctuous to the touch, and neither volatile nor prone to become gummy, it is used to protect substances from contact with air; its non-volatility and power of attracting moisture from the air renders it invaluable for maintaining the moisture of certain bodies, as modeller's clay, dye-stuffs, etc. It is also largely used in weaving, dyeing, calico-printing, printing; to prevent mouldiness in various substances; as a solvent; in the manufacture of nitro-glycerin, dynamite, etc.

Its neutrality, unctuousness, and non-volatility render it applicable to many pharmaceutical uses. As a solvent, in the preparation of *glyceroles*, and of semi-solid cerates, *glycerates;* for the prevention of mould in solutions of morphia, etc., etc.

The glycerin used for medicinal purposes should respond to the following tests: 1st, its specific gravity should not vary much from that given above; 2d, it should not rotate polarized light; 3d, it should not turn brown when heated with sodium hydrate; 4th, it should not be colored by hydrogen sulphide; 5th, when dissolved in its own weight of alcohol containing one per cent. of sulphuric acid, the solution should be clear; 6th, when mixed with an equal volume of sulphuric acid of sp. gr. 1.83, it should form a limpid, brownish mixture, but should not give off gas.

Malic Acid, $C_4H_6O_5$.

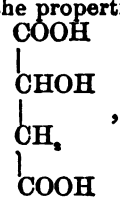
This acid is the only one of those derivable from the glycerin series which is of medical importance. It exists in the vegetable kingdom, either free or in combination with potassium, sodium, calcium, magnesium,

or organic bases; principally in fruits such as apples, cherries, etc.; accompanied by citrates and tartrates.

It may be obtained from the unripe berries of the mountain ash. The expressed juice is heated and calcium carbonate added as long as there is effervescence; the liquid is allowed to cool, filtered, plumbic nitrate added, and set aside until the plumbic nitrate crystallizes. The crystals are slightly washed with cold water, dissolved, the solution decomposed with hydrogen sulphide, filtered, and the filtrate evaporated over the water-bath.

The acid obtained by this process crystallizes in brilliant, prismatic needles; odorless; having a strongly acid taste; fusible at 100°; lose water at 140°; deliquescent, very soluble in water and in alcohol. Its aqueous solution is lævogyrous: $[a]_{D=}$—5°. When heated to 175°—180° malic acid is decomposed into water and *maleic acid.*

There exists another modification of malic acid, formed by the action of nitrous acid upon *aspartic acid,* which differs from this in being optically inactive, in its fusing-point, 133°, and in the properties of its salts.

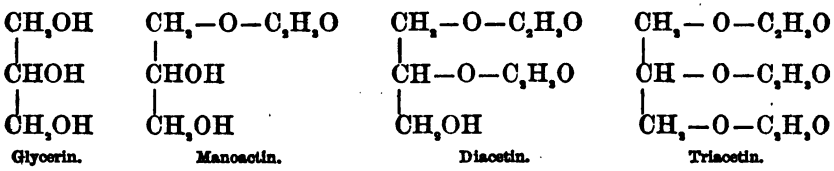
As indicated by the formula of constitution  , malic acid is triatomic and dibasic.

The malates when taken into the economy, are oxidized to carbonates.

ETHERS OF GLYCERIN.

Glycerides.

Being a triatomic alcohol, glycerin contains three groups OH, the hydrogen of each of which may be replaced by an acid radical; or, more properly speaking, one, two, or three of these oxhydryl groups may be removed, leaving a univalent, divalent, or trivalent remainder, which may replace the hydrogen of one, two, or three molecules of a monobasic acid to form three series of ethers:



Of the many substances of this class, only a few, principally those entering into the composition of the neutral fats, require consideration here.

Tributyrin, $C_3H_5(O,C_4H_7O)_3$,—exists in butter. It may also be obtained by heating glycerin with butyric and sulphuric acids. It is a liquid, having a pungent odor and taste; is exceedingly prone to decomposition, with liberation of butyric acid.

Trivalerin, $C_3H_5(O,C_5H_9O)_3$—exists in the oil of some maritime mammalia, and is identical with the *phocenine* of Chevreul.

Tricaproin, $C_3H_5(O,C_6H_{11}O)_3$—**Tricaprylin**, $C_3H_5(O.C_8H_{15}O)_3$, and **Tricaprin**, $C_3H_5(O,C_{10}H_{19}O)_3$,—exist in small quantities in milk, butter and cocoa-butter.

Tripalmitin, $C_3H_5(O,C_{16}H_{31}O)_3$,—exists in most animal and vegetable fats, notably in palm-oil; it may also be obtained by heating glycerin with eight to ten times its weight of palmitic acid for eight hours at 250°. It forms crystalline plates, very sparingly soluble in alcohol, even when boiling; very soluble in ether. It fuses at 50° and solidifies again at 46°.

Trimargarin, $C_3H_5(O,C_{17}H_{33}O)_3$,—has probably been obtained artificially as a crystalline solid, fusible at 60°, solidifiable at 52°. The substance formerly described under this name as a constituent of animal fats is a mixture of tripalmitin and tristearin.

Tristearin, $C_3H_5(O,C_{18}H_{35}O)_3$,—is the most abundant constituent of the solid fatty substances. It is prepared in large quantities as an industrial product in the manufacture of stearin candles, etc., but is obtained in a state of purity only with great difficulty.

In as pure a form as readily obtainable, it forms a hard, brittle, crystalline mass; fusible at 68°, solidifiable at 61°; soluble in boiling alcohol, almost insoluble in cold alcohol, readily soluble in ether.

Triolein, $C_3H_5(O,C_{18}H_{33}O)_3$,—exists in varying quantity in all fats, and is the predominant constituent of those which are liquid at ordinary temperatures, it may be obtained from animal fats by boiling with alcohol, filtering the solution, decanting after twenty-four hours' standing; freezing at 0°, and expressing.

It is a colorless, odorless, tasteless oil; soluble in alcohol and ether, insoluble in water; sp. gr. 0.92.

Trinitro-glycerin — nitro-glycerin — $C_3H_5(ONO_2)_3$. — This substance, which is used as an explosive, both pure and mixed with other substances in dynamite, giant powder, etc., is obtained by the combined action of sulphuric and nitric acids upon glycerin. Fuming nitric acid is mixed with twice its weight of sulphuric acid in a cooled earthen vessel; thirty-three parts by weight of the mixed acids are placed in a porcelain vessel, and five parts of glycerin, of 31° Beaumé, are gradually added with constant stirring, while the vessel is kept well cooled; after five minutes the whole is thrown into five to six volumes of cold water; the nitro-glycerin separates as a heavy oil which is washed with cold water.

Nitro-glycerin is an odorless, yellowish oil; has a sweetish taste; sp. gr. 1.6; insoluble in water, soluble in alcohol and ether; not volatile; crystallizes in prismatic needles when kept for some time at 0°; fuses again at 8°.

When pure nitro-glycerin is exposed to the air at 30° for some time, it decomposes without explosion and with production of glyceric and oxalic acids. When heated to 100° it volatilizes without decomposition; at 185° it boils, giving off nitrous fumes; at 217° it explodes violently; if quickly heated to 257°, it assumes the spheroidal form and volatilizes without explosion. Upon the approach of flame at low temperatures it ignites and burns with slight decrepitations. When subjected to sudden shock, it is suddenly decomposed into carbon dioxide, nitrogen, vapor of water and oxygen, the decomposition being attended with a violent explosion.

In order to render this explosive less dangerous to handle, it is now

usually mixed with some inert substance, usually diatomaceous earth, in which form it is known as *dynamite*, etc.

When taken internally, nitro-glycerin is an active poison, producing effects somewhat similar to those of strychnine; even in drop-doses, diluted, it causes violent headache, fever, intestinal pain, and nervous symptoms. It has been latterly used as a therapeutic agent, and has been used by the homœopaths under the name of *glonoin*.

NEUTRAL OILS AND FATS.

These are mixtures in varying proportions of tripalmitin, tristearin, and triolein, with small quantities of other glycerides, coloring and odorous principles, which are obtained from animal and vegetable bodies. The oils are fluid at ordinary temperatures, the solid glycerides being in solution in an excess of the liquid triolein. The fats, owing to a less proportion of the liquid glyceride, are solid or semi-solid at the ordinary temperature of the air; members of both classes are fluid at sufficiently high temperatures, and solidify when exposed to a sufficiently low temperature. They are, when pure, nearly tasteless and odorless, unctuous to the touch, insoluble in and not miscible with water, upon which they float; combustible, burning with a luminous flame; when rubbed upon paper they render it translucent. When heated with the caustic alkalies or in a current of superheated steam, they are *saponified*, *i. e.*, decomposed into glycerin and a fatty acid. If the saponification be produced by an alkali, the fatty acid combines with the alkaline metal to form a *soap* (*q. v.*).

Most of the fats and many of the oils, when exposed to the air, absorb oxygen, are decomposed with liberation of volatile, fatty acids, and acquire an acid taste and odor, and an acid reaction. A fat which has undergone these changes is said to have become *rancid*. Many of the vegetable oils are, however, not prone to this decomposition. Some of them, by oxidation on contact with the air, become thick, hard and dry, forming a kind of varnish over surfaces upon which they are spread; these are designated as *drying* or *siccative* oils. Others, although they become more dense on exposure to air, become neither dry nor gummy; these are known as *non-drying*, *greasy*, or *lubricating* oils.

Under ordinary conditions, oils and melted fats do not mix with water, and, if shaken with that fluid, form a *temporary* milky mixture, which, on standing for a short time, separates into two distinct layers, the oil floating on the water. In the presence, however, of small quantities of certain substances, such as albumen, pancreatin (*q. v.*), ptyalin, etc., the milky mixture obtained by shaking together oil and water does not separate into distinct layers on standing; such a mixture, in which the fat is held in a *permanent* state of suspension in small globules in a watery fluid, is called an *emulsion*.

Fixed Vegetable Oils.

These substances are designated as "fixed," to distinguish them from other vegetable products having an oily appearance, but which differ from the true oils in their chemical composition and in their physical properties, especially in that they are volatile without decomposition, and are

obtained by distillation, while the fixed oils are obtained by expression, with or without the aid of a moderate heat. The fixed oils form two classes, the *greasy* and *drying* oils (see above).

In testing the purity of the oils, advantage is taken of the specific gravity, point of congelation, and of the action of reagents: 1st, *sulphuric acid*—about twenty drops of the oil are placed on a watch-glass over a white surface, and a drop of concentrated sulphuric acid is added; afterward the whole is stirred with a glass rod; the changes of color observed with the principal oils before and after stirring vary with the different oils. 2d, *Pontet's reagent*, made by dissolving six parts of mercury in 7.5 parts of nitric acid of 36° in the cold. One part of this reagent is well shaken with twelve parts of the oil, and the mixture set aside for twelve hours; the greasy oils are completely solidified, while the drying oils remain fluid. 3d, *Hauchecorne's reagent*—three parts of nitric acid of 40°, diluted with one part of distilled water; one gram of this reagent is mixed with three grams of the oil and shaken in a test-tube.

Palm-oil is the product of a species of palm growing on the Guinea coast, in the West Indies, and South America. It is a reddish yellow solid at ordinary temperatures, has a bland taste and an aromatic odor. It saponifies readily, and is used in the manufacture of palm-soap. It is usually acid, and contains free glycerin from spontaneous decomposition.

Rape-seed oil and *colza-oil* are produced from the seeds of various species of *Brassica;* yellow, limpid oils, having a strong odor and a disagreeable taste. They are used for burning in lamps and for the manufacture of soft-soaps.

Croton-oil—*Oleum tiglii* (U. S.)—*Oleum crotonis* (Br.)—is one of the few fixed oils possessed of distinct medicinal properties. It varies much in color and activity, according to its source; that which is obtained from the East is yellowish, liquid, transparent, and much less active than that prepared in Europe from the imported seeds, which is darker, less fluid, caustic in taste, and wholly soluble in absolute alcohol. Croton-oil contains, besides the glycerides of oleic, crotonic and fatty acids, about four per cent. of a peculiar principle called by Schlippe *crotonol*, to which the oil owes its vesicating properties; it also contains an alkaloid-like substance, also existing in castor-oil, called *ricinine*. None of these bodies, however, are possessed of the drastic powers of the oil itself.

Peanut-oil—*Ground-nut oil*—an almost colorless oil, very much resembling olive-oil, in place of which it is frequently used for culinary purposes, intentionally or otherwise. It is readily saponifiable, yielding two peculiar acids, *arachaïc* and *hypogaïc* (see Olive-oil).

Cocoanut-oil or *butter*, not to be confounded with cocoa-butter, is at ordinary temperatures a white solid resembling lard; fuses at about 20°, and solidifies at about 10°; it has a pleasant odor and a bland taste. It is readily saponifiable, yielding a hard sodium soap. It easily becomes rancid. It is said to contain an acid, called *cocinic*, or *cocostearic*.

Almond-oil—*Oleum amygdalæ dulcis* (U. S.)—*Oleum amygdalæ* (Br.)—a light yellow oil, very soluble in ether, soluble in twenty-four parts of alcohol; nearly inodorous; has a bland, sweetish taste. It is largely used in pharmacy, in the preparation of ointments, and in the arts in soap manufacture. The pure oil has no odor of bitter almonds; is completely solidified by Pontet's reagent; is colored peach-red, but not green, by a mixture of nitric and sulphuric acids; produces no coloration when its ethereal solution is shaken with a concentrated alcoholic solution of silver nitrate, and the mixture set aside in the dark for twelve hours.

Olive-oil—Oleum olivæ (U. S., Br.)—a well-known oil of a yellow or greenish yellow color, almost odorless, and of a bland and sweetish taste. The finest grades have a yellow tinge and a faint taste of the fruit; they are prepared by cold pressure; they are less subject to rancidity than the lower grades. Olive-oil is very frequently adulterated, chiefly with poppy-oil, sesame-oil and peanut-oil; the presence of the first is detected by Pontet's reagent, which converts pure olive-oil into a solid mass, while an oil adulterated with a drying oil remains semi-solid. A contamination with oil of sesame is indicated by the production of a green color, with a mixture of nitric and sulphuric acids. Peanut-oil, an exceedingly common adulterant in this country, is recognized by the point of congelation, or more delicately by the following method: ten grams of the oil are saponified; the soap is decomposed with hydrochloric acid; the liberated fatty acids dissolved in 50 c.c. of strong alcohol; the solution precipitated with lead acetate; the precipitate washed with ether; the residue decomposed with hot dilute hydrochloric acid; the oily layer separated and extracted with strong alcohol; the alcoholic fluid, on evaporation, yields crystals of *arachaïc acid*, if the oil contains peanut-oil.

Cotton-seed oil is also added to olive-oil in this country; its presence is detected, like that of other drying oils, by the formation of a pasty magma in place of a solid mass when the oil is subjected to the action of Pontet's reagent.

Cocoa-butter—Oleum theobromæ (U. S., Br.)—is at ordinary temperatures a whitish or yellowish solid of the consistency of tallow, and having an odor of chocolate and a pleasant taste; it does not easily become rancid. The most reliable test of its purity is its fusing-point, which should not be much below +33°.

Linseed-oil—Flaxseed-oil—Oleum lini (U. S., Br.)—is prepared on a large scale as an industrial product, and is largely used by painters. Its drying qualities are increased by charging it with lead oxide, by boiling with litharge (boiled oil). The raw oil has a disagreeable odor and a nauseous taste, is dark yellowish brown in color, and readily soluble in ether and hot alcohol. In this oil oleic acid is, at least partially, replaced by another fluid acid, *linoleic acid*, which, when exposed to the air, gradually absorbs oxygen and becomes thick and finally solid.

Castor-oil—Oleum ricini (U.S., Br.)—is usually obtained by expression of the seeds, although in some countries it is prepared by decoction or by extraction with alcohol. It is a thick, viscid, yellowish oil, has a faint odor and a nauseous taste. It is more soluble in alcohol than any other fixed vegetable oil, and is also very soluble in ether. It saponifies very readily. Ammonia separates from it a crystalline solid, fusible at 66°—*ricinolamide*. Hot nitric acid attacks it energetically, and finally converts it into *suberic acid*.

Animal Oils.

The principal oils of animal origin used in the arts and in medicine are the following:

Whale-oil—Train-oil—obtained by *trying out* the fat or blubber of the "right whale" and of other species of *balænæ*. It is of sp. gr. 0.924; at 15°; brownish in color; becomes solid at about 0°; has a very nauseous taste and odor; it may be deodorized to a certain extent by passing through it a current of steam heated to 160°. It is colored yellow by sulphuric

acid; with Pontet's reagent it forms a yellow salve, which slowly turns brown; chlorine blackens it immediately.

Sperm-oil is obtained, along with spermaceti, from the cranial cavities of the cachalot or sperm-whale. It is a clear, transparent, orange-yellow oil; sp. gr. 0.884 at 15°; at — 8° it deposits crystals of a solid fat. It saponifies with difficulty, and is solidified by Pontet's reagent.

Porpoise-oil; a pale yellow, neutral oil; sp. gr. 0.937 at 16°; solidifies at —15°.

Dolphin-oil; a pale yellow, neutral oil; sp. gr. 0.918 at 20°; when cooled it deposits crystals at +5° and again at —3°.

Seal-oil; a dark brown, viscid oil, having a disgusting odor; sp. gr. 0.9317 at 11°.

Shark-oil; a pale yellow, stinking oil of sp. gr. 0.870 at 15°.

These oils are used in the manufacture of soft soaps, for illumination, and in dressing leather.

Neat's-foot oil— Oleum bubulum (U.S.)—is obtained by the action of boiling water upon the feet of neat cattle, horses, and sheep, deprived of the flesh and hoofs. It is straw yellow or reddish yellow, odorless, not disagreeable in taste, not prone to rancidity, does not solidify at quite low temperatures; sp. gr. at 15°, 0.916. It is bleached, not colored, by chlorine; in which it differs from fish- and whale-oils. It is used as a lubricant and in pharmacy.

Lard-oil, obtained in large quantities in the United States as a by-product in the manufacture of candles, etc., from pigs' fat. A light yellow oil, used principally as a lubricant; it is not colored by sulphuric acid, but is colored brown by a mixture of sulphuric and nitric acids.

Tallow-oil—obtained by expression with a gentle heat from the fat of the ox and sheep. Sp. gr. 0.9003; light yellow in color. Colored brown by sulphuric acid. Formerly this oil, under the trade-name of "oleic acid," was simply a by-product in the manufacture of stearine candles; of late years, however, it is specially prepared for the manufacture of oleo-margarine.

Cod-liver oil— Oleum morrhuæ (U. S., Br.)—is obtained principally in Norway and Newfoundland, from the livers of codfish, either by extraction with water heated to about 80°, or by hanging the livers in the sun and collecting the oil which drips from them. There are three commercial varieties of this oil: *a. Brown.*—Dark brown, with greenish reflections; sp. gr. 0.928 at 15°; has a disagreeable, irritating taste; faintly acid; does not solidify at —13°. *b. Pale brown.*—Of the color of Malaga wine; sp. gr. 0.924; has a peculiar odor and a fishy, irritating taste; strongly acid. *c. Pale.*—Golden yellow; sp. gr. 0.928 at 15°; deposits a white fat at —13°; has a fresh odor, slightly fishy, and a not unpleasant taste, without after-taste.

Pure cod-liver oil, with a drop of sulphuric acid, gives a bluish violet aureole, which gradually changes to crimson, and later to brown. A drop of fuming nitric acid dropped into the oil is surrounded by a pink aureole if the oil be pure; if largely adulterated with other fish-oils, the pink color is not observed and the oil becomes slightly cloudy. Fresh cod-liver oil is not colored by rosaniline. If a third of the oil is distilled, the distillate becomes solid; while if it be contaminated with vegetable oils, the distillate becomes liquid.

Cod-liver oil contains, besides the glycerides of oleic, palmitic and stearic acids, those of butyric and acetic acids, certain biliary principles (to whose presence the sulphuric acid reaction given above is probably

due), a phosphorized fat of undetermined composition, small quantities of bromine and iodine, probably in the form of organic compounds, a peculiar fatty acid called *gadinic acid,* which solidifies at 60°, and a brown substance called *gaduin* or *gadinine.*

To which, if to any of these substances, cod-liver oil owes its value as a therapeutic agent, is still unknown, although many theories have been advanced. Certain it is, however, that one of the chief values of this oil is as a food in a readily assimilable form.

SOLID ANIMAL FATS.

Condition in the body.—The glycerides of stearic, palmitic and oleic acids exist, in health, in all, or nearly all, parts of the body; in the fluids in solution or in suspension, in the form of minute oil-globules; incorporated in the solid or semi-solid tissues, or deposited in collections in certain locations, as under the skin, inclosed in cells of connective tissue, in which the mixture of the three glycerides is in such proportion that the contents of the cells are fluid at the temperature of the body.

The total amount of fat in the body of a healthy adult is from 2.5 to 5 per cent. of the body-weight, although it may vary considerably from that proportion in conditions not, strictly speaking, pathological. The approximate quantities of fat in 100 parts of the various tissues and fluids, in health, are the following:

Urine	?	Blood	0.4	Cortex of brain	5.5
Perspiration	0.001	Cartilage	1.8	Brain	8.0
Vitreous humor	0.002	Bone	1.4	Hen's egg	11.6
Saliva	0.02	Bile	1.4	White matter of brain	20.0
Lymph	0.05	Crystalline lens	2.0	Nerve-tissue	22.1
Synovial fluid	0.06	Liver	2.4	Spinal cord	23.6
Amniotic fluid	0.2	Muscle	3.3	Fat-tissue	82.7
Chyle	0.3	Hair	4.2	Marrow	96.0
Mucus	0.4	Milk	4.3		

The amount of fat in the body, under normal conditions, is usually greater in women and children than in men; generally greater in middle than in old age, although in some individuals the reverse is the case; greater in the inhabitants of cold climates than in those of hot countries.

In wasting from disease and from starvation the fats are rapidly absorbed, and are again as rapidly deposited when the normal condition of affairs is restored.

Besides as a result of the tendency to corpulence, which in some individuals amounts to a pathological condition, fats may accumulate in certain tissues as a result of morbid changes. This accumulation may be due either to degeneration or to infiltration. In the former case, as when muscular tissue degenerates in consequence of long disuse, the natural tissue disappears and is replaced by fat; in the latter case, as in fatty infiltration of the heart, oil-globules are deposited between the natural morphological elements, whose change, however, may subsequently take place by true fatty degeneration due to pressure. Fatty degeneration of the liver and of other organs occurs also in phthisis, chronic heart and lung affections, as a result of overfeeding, from the abuse of alcoholic stimulants, and from the action of certain poisons, especially of phosphorus. Tumors composed of adipose tissue occur and are known as "lipomata."

The greater part of the fat of the body enters it as such with the food; not unimportant quantities are, however, formed in the body, and that from the albuminoid as well as from the starchy and saccharine constituents of the food. By what steps this transformation takes place is still uncertain, although there is abundant evidence that it does occur.

Those fats taken in with the food are unaltered by the digestive fluids, except in that they are freed from their enclosing membranes in the stomach, until they reach the duodenum; here, under the influence of the pancreatic juice, the major part is converted into a fine emulsion, in which form it is absorbed by the lacteals. A smaller portion is saponified, and the products of the saponification, free fatty acids, soaps, and glycerin, subsequently absorbed by lacteals and blood-vessels.

The service of the fats in the economy is undoubtedly as a producer of heat and force by its oxidation; and by its low power of conducting heat, and the position in which it is deposited under the skin, as a retainer of heat produced in the body. The fats are not discharged from the system in health, except the excess contained in the food over that which the absorbents are capable of taking up, which passes out with the fæces, a small quantity distributed over the surface in the perspiration and sebaceous secretion (which can hardly be said to be eliminated) and a mere trace in the urine.

Animal Fats used in the Arts and in Pharmacy.—The principal of these are *lard*, *tallow*, and *butter*.

Lard—Adeps (U. S.)—is the fat of the hog freed from connective tissue. It is white, almost odorless, almost tasteless, soft; fusible at 38°; readily saponifiable by alkalies; not prone to rancidity if properly prepared.

Tallow, the purified fat of the ox or sheep; is rather harder than lard; white, tasteless, and odorless when pure; fuses at about 44°; and solidifies at about 37°.

Butter, the fat of milk, separated and made to agglomerate by agitation, and more or less salted to insure its keeping. It consists of the glycerides of stearic, palmitic, oleic, butyric, capric, caprylic, and caproic acids, with a small amount of coloring matter, more or less water and salt and casein. Good, natural butter contains eighty to ninety per cent. of fat, six to ten per cent. of water, two to five per cent. of curd, and two to five per cent. of salt; fuses at from 32.8° to 34.9°.

Butter is very liable to adulterations, the chief adulterants being excess of water and salt, starch, animal fats other than those of butter, artificial coloring matters.

Excess of salt and water are usually worked in together, the former up to fourteen per cent. and the latter to fifteen per cent. To determine the presence of an excess of water, about four grams of the butter, taken from the middle of the lump, are weighed in a porcelain capsule, in which it is heated over the water-bath, as long as it loses weight; it is then weighed again; the loss of weight is that of the quantity of water in the original weight of butter, less that of the capsule. The proportion of salt is determined by incinerating a weighed quantity of butter and determinmining the chlorine in the ash by the nitrate of silver method (see Sodium Chloride). Roughly, the weight of the ash may be taken as salt. Starch is detected by spreading out a thin layer of the butter, adding solution of iodine, and examining under the microscope for purple spots.

To determine the presence of foreign fats, the best method is that of Angell and Hehner. A pear-shaped bulb is made by blowing a small globe in the end of a piece of glass tubing of one-fourth inch diameter

and drawing off a tapering neck very near the bulb, the diameter of which should be about one-half inch; enough mercury is then placed in the bulb to make the whole weigh 3.4 grams, and the open end closed by fusion. To use this little apparatus, twenty to thirty grams of the butter to be tested are melted in a beaker on the water-bath, and, when quite fluid, poured into a test-tube three-fourths inch in internal diameter and six inches long, until the tube is filled to within two inches of the top; the tube is then kept warm and upright until the fat has separated in a clear layer above the water, etc., after which it is solidified by immersion in water at 15°; the surface should only be slightly depressed. The test-tube with the solidified butter is suspended in a large beaker of cold water; the small bulb is laid upon the surface of the fat, which should be one and one-half inch below the surface of the water in the beaker, and a thermometer is suspended near the test-tube. The water is now heated until the globular part of the bulb has just sunk below the surface of the fat, at which point the standing of the thermometer is read off; this is the "sinking-point" of the butter, and should be from 34.3° to 36.3°. Oleomargarine, or butterine, has a lower sinking-point, and butter adulterated with fats a higher one.

Soaps.

These compounds, which have been known from time immemorial, are the metallic salts of stearic, palmitic, and oleic acids; those of potassium, sodium, and ammonium are soluble in water, while those of other metals are insoluble; those of potassium and sodium are also soluble in alcohol and in ether. The sodium soaps are hard, and those of potassium soft.

Soap is made from almost any oil or fat, the best from olive-oil, or peanut- or palm-oil, and lard. The first step in the process of manufacture is the *saponification* of the fat, which consists in the decomposition of the glyceric ethers into glycerin and the fatty acids, and the combination of the latter with an alkaline metal; it is usually effected by gradually adding the fluid fat to a weak boiling solution of caustic soda or potassa to saturation. From this weak solution the soap is separated by "salting," which consists in adding, during constant agitation, a solution of caustic alkali, heavily charged with common salt, until the soap separates in grumous masses, which float upon the surface and are separated. Finally the soap is pressed to separate adhering water, fused, and cast into moulds.

The varieties of soaps used in the arts and in medicine are numerous.

Yellow soap is made from tallow or other animal fat, and about one-third weight of rosin subsequently added.

White castile soap—*Olive-oil soap* (*Sapo*, U. S.; *Sapo durus*, Br.), is pale grayish white in color, hard, dry, not greasy; strongly alkaline; very soluble in alcohol and water; contains twenty-one per cent. of water. A marbled variety of the same soap is made by using a soda containing ferruginous matter and agitating the saponified fat at the proper time; it is harder than the white variety, and contains less water—fourteen per cent. A soft or potash soap is also made from olive-oil, and, like other soft soaps, contains an excess of alkali and glycerin; it is the *Sapo mollis* (U. S.). Olive-oil soaps are usually imported from France and Spain.

Almond-oil soap is the officinal soap of the French Codex, and contains glycerin and an excess of alkali.

Emplastrum plumbi (U. S., Br.) is simply a lead-soap, prepared by saponifying olive-oil, or a mixture of olive-oil and lard with litharge.

Linimentum calcis (U. S., Br.) is a mixture of calcium soap with olive- or flaxseed-oil in excess.

All the soaps are decomposed by even weak acids, with liberation of the fatty acids; by compounds of the alkaline earths, with formation of an insoluble soap; and in the same way by most of the metallic salts.

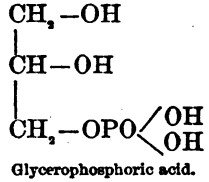
Phosphorized Fats.

Lecithins.—That brain-tissue contains phosphorus was known as early as 1779, and that this phosphorus exists in combination in a fat-like material was determined in the early part of the present century. In 1851 Gobley described a fatty material which he obtained from the yolks of eggs, and which he called *lecithin;* later, in 1865, Liebreich described a substance also containing phosphorus, which he obtained from brain-tissue, and which he designated as *protogon.*

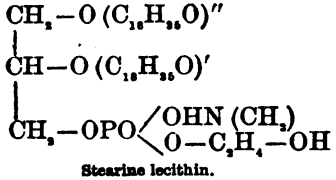
Most later authors have considered protogon as being a mixture of lecithin and another substance called *cerebrin,* although Gamgee advances strong grounds for its admission as a distinct substance. The study of the constituents of brain- and nerve-tissue is one surrounded with great difficulties, and has led as yet to but few results sufficiently well established for adoption in a work of this nature.

That *lecithin,* however, or rather a number of lecithins, exist in brain-tissue, in the yolks of hens' eggs, in fish-roes, etc., may be considered as definitely settled.

These substances are of very complex constitution; they yield, on decomposition, *neurine* (see p. 206), stearic, palmitic, or oleic acid, and a peculiar acid, called from its composition, *glycerophosphoric acid.* They are, therefor, glycerophosphoric acid in which the remaining hydrogens of the glycerin are replaced by radicals of fatty acids, and the remaining oxhydryls of the phosphoric acid by neurine:



Glycerophosphoric acid.



Stearine lecithin.

The lecithins are yellowish white, waxy, hygroscopic solids, imperfectly crystalline, soluble in ether and alcohol, insoluble in water, in which they swell like starch; when ignited they burn, leaving a residue of metaphosphoric acid and carbon. They form compounds with certain salts, as platinic chloride, and with acids. They are readily decomposed, yielding the products mentioned above.

THIRD SERIES OF HYDROCARBONS.

SERIES C_nH_{2n-2}.

The terms of this series at present known are:

Acetylene	C_2H_2	Crotonylene	C_4H_6	Rutylene	$C_{10}H_{18}$
Allylene	C_3H_4	Valerylene	C_5H_8	Benylene	$C_{15}H_{28}$

Acetylene.

Ethene, C_2H_2—was discovered by Davy. It exists as a constituent of coal-gas; it is formed as a product of the decomposition, by heat and otherwise, of a number of organic substances, notably of hydrocarbons, ether, chloroform, etc. It is best prepared by passing a slow current of coal-gas through a narrow tube through which induction sparks are passing, directing the gas through a solution of cuprous chloride, and collecting and decomposing the precipitate with hydrochloric acid.

A most interesting method of its formation is that by direct synthesis, discovered by Berthelot: a slow current of hydrogen is passed through a glass globe in which are the carbon-points of an electric light; the escaping gas contains acetylene formed by the direct union of carbon and hydrogen.

Acetylene is a colorless gas, rather soluble in water; it has a peculiar, disagreeable odor, which is observed when a Bunsen burner burns within the tube, and when a piece of platinum foil is incandescent in vapor of ether; it burns with a white, luminous flame.

When mixed with oxygen it explodes violently on the approach of a flame, a deposit of carbon being formed if the amount of oxygen be deficient. It unites with nitrogen under the influence of the electric discharge, to form hydrocyanic acid. It combines with hydrogen to form ethylene. Mixed with chlorine it detonates violently even in diffuse daylight, and without the application of heat. It may be made to unite with itself to form its superior polymeres:

C_2H_2	C_6H_6	C_8H_8	$C_{10}H_{10}$
Acetylene.	Benzene.	Styrolene.	Naphthydrene.

Its most characteristic property is that of forming a blood-red precipitate of cuproso-acetyl oxide when it is passed through an ammoniacal solution of cuprous chloride, a reaction by which the presence of traces of this gas may be detected; similar compounds are formed with other metals. These precipitates, when dried, explode violently when subjected to shock, and it is probable that explosions which sometimes occur without any apparent cause, in pipes through which illuminating-gas is conducted, especially if of brass or copper, are due to their formation.

Illuminating-Gas.

Illuminating-gas is now manufactured by a variety of processes, almost every gas company using some peculiar modification of the method, or of the nature and proportion of the raw materials; thus, we have gas made from wood, from coal, from fats, from petroleum, and by

the decomposition of water and subsequent charging of the gas with the vapor of naphtha. The typical process is that in which the gas is produced by heating cannel or other bituminous coal to bright redness in retorts. As it issues from the retorts, the gas is charged with substances volatile only at high temperatures; these are deposited in the condensers or coolers, and form coal- or gas-tar. From the condensers the gas passes through what are known as "scrubbers" and "lime-purifiers," in which it is deprived of ammoniacal compounds and other impurities. As it comes from the condensers, coal-gas contains:

* Acetylene.	* Styrole.	‡ Hydrogen.	† Hydrogen sulphide.
* Ethylene.	* Naphthalene.	† Carbon monoxide.	† Carbon disulphide.
* Marsh-gas.	* Acenaphthalene.	† Carbon dioxide.	† Sulphuretted hydrocarbons.
* Butylene.	* Fluorene.	† Ammonia.	† Nitrogen.
* Propylene.	* Propyl hydride.	† Cyanogen.	† Aqueous vapor.
* Benzene.	* Butyl hydride.	† Sulphocyanogen.	

In passing through the purifiers the gas is freed of the impurities to a greater or less extent, and, as usually delivered to consumers, contains:

* Marsh-gas.	* Ethylene.	† Nitrogen	† Carbon monoxide.
* Acetylene.	‡ Hydrogen.	† Aqueous vapor.	† Carbon dioxide.

* Vapors of hydrocarbons.

Allylene, C_3H_4—is a colorless gas, very soluble in alcohol, quite soluble in water; has a slightly less disagreeable odor than acetylene; burns with a smoky flame. It is obtained by a general reaction used for the obtaining of hydrocarbons of this series, which consists in heating the monobromine compounds of the corresponding hydrocarbon of the ethylene series with sodium ethyl oxide:

$$\underset{\text{Monobrom-ethylene.}}{C_2H_3Br} + \underset{\text{Sodium ethyl oxide.}}{C_2H_5NaO} = \underset{\text{Sodium bromide.}}{NaBr} + \underset{\text{Alcohol.}}{C_2H_5HO} + \underset{\text{Acetylene.}}{C_2H_2}$$

$$\underset{\text{Monobrom-propylene.}}{C_3H_5Br} + \underset{\text{Sodium ethyl oxide.}}{C_2H_5NaO} = \underset{\text{Sodium bromide.}}{NaBr} + \underset{\text{Alcohol.}}{C_2H_5HO} + \underset{\text{Allylene.}}{C_3H_4}$$

It is distinguished from acetylene by forming a gray precipitate with mercurous salts, a white one with the silver salts, and a yellow one with the cuprous salts.

Crotonylene, C_4H_6—obtained by the general method from monobrombutylene. It is liquid below 15°; boils at about 18°; has a powerful and somewhat alliaceous odor; burns with a bright, smoky flame. It has also been obtained by distilling erythrite (*q. v.*) with formic acid.

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* Illuminating constituents. † Impurities. ‡ Diluent.

TETRATOMIC ALCOHOLS.

Very few of these compounds have yet been obtained. They may be regarded as the hydrates of the hydrocarbons C_nH_{2n-2}; as the glycols are the hydrates of the ethylene series.

Propylphycite, $C_3H_4(OH)_4$,—is probably the first term of the series, although its existence is not yet well established.

Erythrite—*phycite*—$\begin{matrix}CH_2OH\\|\\CHOH\\|\\CHOH\\|\\CH_2OH\end{matrix}$ $=C_4H_6(OH)_4$—a well-defined compound, was discovered in 1848, as a product of decomposition of *erythrine*, $C_{20}H_{22}O_{10}$, which exists in lichens of the genus *rocella*. To obtain it the lichens are macerated in water; treated with powdered lime; the solution filtered after half an hour; the filtrate treated with hydrochloric acid; the gelatinous precipitate of erythrine is washed, dried, and introduced into a Papin's digester with a small quantity of slacked lime, and heated to 100° for two hours; the liquid is filtered and slowly evaporated; *orcine* separates first and is removed, afterward erythrite, which is purified by recrystallization from boiling alcohol.

Erythrite crystallizes in large, brilliant prisms; very soluble in water and in hot alcohol, almost insoluble in ether; it is sweetish in taste; its solutions neither affect polarized light, nor reduce Fehling's solution, nor are capable of fermentation; it fuses at 120°, and at 300° is partly decomposed, giving off an odor of caramel. Its watery solution, like that of sugar, is capable of dissolving a considerable quantity of lime, and from this solution alcohol precipitates a definite compound of erythrite and calcium. By oxidation with platinum black it yields *erythroglucic acid*, $C_4H_8O_5$. With fuming nitric acid it forms a tetranitro compound, which explodes under the hammer.

ACIDS DERIVABLE FROM ERYTHRITE.

Theoretically erythrite should, by simple oxidation, yield two acids; one of the series $C_nH_{2n}O_5$, and another of the series $C_nH_{2n-2}O_6$. Although both of these acids are known, only the first, *erythroglucic acid*, has been obtained by oxidation of erythrite:

$\begin{matrix}CH_2OH\\\|\\CHOH\\\|\\CHOH\\\|\\CH_2OH\end{matrix}$	$\begin{matrix}COOH\\\|\\CHOH\\\|\\CHOH\\\|\\CH_2OH\end{matrix}$	$\begin{matrix}COOH\\\|\\CHOH\\\|\\CHOH\\\|\\COOH\end{matrix}$
Erythrite.	Erythroglucic acid.	Tartaric acid.

Tartaric Acids.

Acidum tartaricum (U. S., Br.), $C_4H_6O_6$.—There exist four acids having the composition $C_4H_6O_6$; which differ from each other only in their physical properties, and are very readily converted one into another; they are designated as: 1st, *Right;* 2d, *Left;* 3d, *Inactive tartaric acid;* 4th, *Racemic acid. Right* or *Dextrotartaric acid* crystallizes in large, oblique, rhombic prisms, having hemihedral facettes. Solutions of the acid and its salts are dextrogyrous.

Left or *Lævotartaric acid* crystallizes in the same form as dextrotartaric acid, only the hemihedral facettes are on the opposite sides, so that crystals of the two acids, when held facing each other, appear like the reflections one of the other. Its solution and those of its salts are lævogyrous to the same degree that corresponding solutions of dextrotartaric acid are dextrogyrous.

Racemic acid is a compound of the two preceding; it forms crystals having no hemihedral facettes, and its solutions are without action on polarized light. It is readily separated into its components.

Inactive tartaric acid, although resembling racemic acid in its crystalline form and inactivity with respect to polarized light, differs essentially from that acid in that it cannot be decomposed into right and left acids, and in the method of its production.

The tartaric acid which exists in nature is the dextrotartaric; it occurs, both free and in combination, in the sap of the vine and in a great number of other vegetable juices and fruits; it has not been detected as a constituent of animal bodies. Although this is probably the only tartaric acid existing in nature, all four varieties may and do occur in the commercial acid, being formed during the process of manufacture.

Tartaric acid is obtained in the arts from hydropotassic tartrate, or cream of tartar (*q. v.*). This salt is dissolved in water and the solution boiled with chalk until its reaction is neutral; calcic and potassic tartrates are formed:

$$\underset{\text{Hydro-potassic tartrate.}}{2(C_4H_4O_6,HK)} + \underset{\text{Calcium carbonate.}}{CO_3Ca} = \underset{\text{Calcium tartrate.}}{C_4H_4O_6Ca} + \underset{\text{Potassic tartrate.}}{C_4H_4O_6K_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2}$$

The insoluble calcic salt is separated and the potassic salt decomposed by treating the solution with calcic chloride:

$$\underset{\text{Potassic tartrate.}}{C_4H_4O_6K_2} + \underset{\text{Calcium chloride.}}{CaCl_2} = \underset{\text{Calcium tartrate.}}{C_4H_4O_6Ca} + \underset{\text{Potassium chloride.}}{2KCl}$$

The united deposits of calcium tartrate are suspended in water, decomposed with the proper quantity of sulphuric acid, the solution separated from the deposit of calcium sulphate, and evaporated to crystallization.

The commercial acid is liable to contamination with sulphuric acid, lead and calcium compounds, from which it may be freed by recrystallization. When sufficiently pure for pharmaceutic purposes, its solution is not affected by hydrogen sulphide, and gives no preciptate with calcium sulphate or ammonium oxalate, and with barium chloride no precipitate not entirely soluble in nitric acid. It should not attract moisture from

the air, should be entirely soluble in alcohol, and should be entirely consumed when heated to redness as platinum foil.

The ordinary tartaric acid crystallizes in large prisms; very soluble in water and in alcohol, insoluble in ether; permanent in air; acid in taste and reaction. Its solutions become mouldy on standing.

It fuses at 170°; at 180° it loses water and is gradually converted into an anhydride; at 200°—210° the acid is decomposed with formation of new volatile products, *pyruvic* and *pyrotartaric acids;* at higher temperatures the decomposition is more complete, and results in the production of acetic acid, carbon dioxide and monoxide, water, hydrocarbons and charcoal; if still further heated in air, it burns with an odor of caramel. If kept in fusion for some time, two molecules of the acid unite, with loss of the constituents of a molecule of water, to form *tartralic* or *ditartric acid*, $C_8H_{10}O_{11}$.

Tartaric acid is attacked by oxidizing agents with formation of carbon dioxide, water, and, in some instances, formic and oxalic acids. Certain reducing agents convert it into malic and succinic acids. With fuming nitric acid it forms a dinitro-compound, which is very unstable, and which, when decomposed below 36°, yields tartaric acid. It forms a precipitate with lime-water, soluble in an excess of water; in not too dilute solution it forms a precipitate with potassium sulphate solution; it does not precipitate with the salts of calcium. When heated with a solution of auric chloride it precipitates the gold in the metallic form.

As its formula indicates (see above), tartaric acid is tetratomic and dibasic; it forms many salts which are of medical importance, and exhibits a great tendency to the formation of double salts, such as tartar emetic (*q. v.*).

When taken into the economy, as it constantly is in the form of tartrates, the greater part is oxidized to carbonic acid (carbonates); but, if taken in sufficient quantity, a portion is excreted unchanged in the urine and perspiration. The free acid is poisonous in large doses.

In pharmacy tartaric acid is used chiefly in effervescent mixtures, seidlitz powder, etc., and is frequently used in place of the more costly citric acid. In the arts it is extensively consumed in processes of dyeing.

There exist anhydrides, ethers, and amides corresponding to the tartaric acids, none of which is of medical interest.

Citric Acid, $C_6H_8O_7+Aq$,

is best considered in this place, although its constitution is different from that of tartaric acid. It exists in the acid juices of many fruits—lemon, strawberry, gooseberry, cherry, orange, etc.

It is obtained from lemon-juice, which is filtered, boiled, and saturated with chalk. The insoluble calcium citrate is separated and decomposed with sulphuric acid, the solution filtered, and evaporated to crystallization.

It crystallizes in large, right rhombic prisms, which lose their aq. at 100°; very soluble in water, less soluble in alcohol, sparingly soluble in ether; heated to 100° it fuses; at 175° it is decomposed, with loss of water and formation of *aconitic acid*, $C_6H_6O_6$; at a higher temperature, carbon dioxide is given off, and *itaconic acid*, $C_5H_6O_4$, and *citraconic acid*, $C_5H_6O_4$, are formed.

Concentrated sulphuric acid decomposes it with evolution of carbon

monoxide; oxidizing agents convert it into formic acid and carbon dioxide; or into carbon dioxide and acetone; or into oxalic and acetic acids and carbon dioxide. It is tetratomic and tribasic.

PENTATOMIC ALCOHOLS.

Only two of these compounds are known, and require mere mention.

Quercite, $C_6H_{12}O_5$—a sugar-like substance obtained from acorns. It forms hard crystals, soluble in water and in hot aqueous alcohol; permanent in air; fuses at a temperature above 235°, and sublimes with a slight darkening in color. It is not affected by the alkalies; does not reduce Fehling's solution, and is not fermentable; with a mixture of nitric and sulphuric acids it yields a detonating nitro-compound.

Pinite is an isomere of quercite, obtained from the exudations of California pine (*Pinus Lambertiana*). It crystallizes in hard, white, mamellated masses; very soluble in water, almost insoluble in alcohol and ether; its solution is dextrogyrous, $[a]_D = +58.6°$; it fuses without decomposition at 150°. It reduces solutions of silver nitrate, but not Fehling's solution; nor is it capable of fermentation.

FOURTH SERIES OF HYDROCARBONS.

Series C_nH_{2n-4}.

But one of the lower terms of this series is known; this is *valylene*, C_5H_6, obtained by the action of an alcoholic solution of potash on valerylene dibromide. It is a liquid, boiling at 45°.

Among the higher terms of the series are many substances of industrial and medical importance.

Terebenthene, $C_{10}H_{16}$, is the type of a great number of isomeric substances existing in the *volatile oils* or *essences*. It is the chief constituent of oil of turpentine.

To obtain it in a state of purity, oil of turpentine is mixed with an alkaline carbonate, and distilled in vacuo over a water-bath, or by fractional distillation of the crude oil, those portions being collected which pass over at about 156°.

Pure terebenthene is a colorless, mobile liquid; has the peculiar odor of turpentine; boils at about 156°; burns with a smoky, luminous flame; obtained from the turpentine of *pinus maritima*, it is lævogyrous, purified by distillation in vacuo, $[a]_D = -42.36°$, by fractional distillation, $[a]_D = -40.32°$; that obtained from *pinus australis* is dextrogyrous, $[a]_D = +18.9°$; specific gravity at $0° = 0.8767$.

It absorbs oxygen rapidly from the air, whether pure or in the commercial essence, becoming thick and finally gummy. Oxidizing agents, such as nitric acid, attack it energetically, causing it to ignite and burn suddenly, with separation of a large volume of carbon. Hydrochloric acid unites with it to form a number of compounds, as do also hydriodic and hydrobromic acids—all the compounds having the odor of camphor. When mixed with nitric acid diluted with alcohol and exposed to the air, it forms a crystalline pseudo-glycol, *terpine*. Chlorine, bromine, and iodine form compounds of substitution or of addition.

Turpentine—Terebenthina (U. S.)—is the name given to the concrete juice of various species of trees of the genera *Pinus*, *Abies*, and *Larix*, which consists of terebenthene, its isomeres, and resinous and other substances. The product differs in composition and properties according to the kind of tree from which it is produced; the varieties recognized by the United States Dispensatory are the following:

First.— White turpentine—Common American turpentine—obtained in North Carolina and adjacent States, from *Pinus palustris* and *P. tœda*. It is yellowish white, semi-fluid at summer temperature, hard and solid when cooled; on exposure to air it becomes dry, hard, and brittle. It is usually subjected to distillation near the place of its collection, by which process it is separated into the volatile *oil*, or *essence of turpentine* (*q. v.*), and *resin*, or *colophony* (*q. v.*).

Second.—European turpentine—Bordeaux turpentine—obtained in the south of France, etc., from *P. sylvestris* and *P. maritima*, is the variety principally used in Europe, but rarely finds its way to this country.

Third.— Canada turpentine—Canada balsam—Balsam of fir—is produced in Canada and Maine from *abies balsamea*. It is a tenacious semi-solid, of the consistency of honey when fresh, colorless or yellowish, sticky, bitter in taste, and having a balsamic odor; when long exposed to the air, or when heated over the water-bath, its volatile constituents are lost, and it is converted into a hard, brittle mass.

Fourth.— Venice turpentine—produced principally in Switzerland from *larix Europœa*. It is a thick, viscid liquid, yellowish or greenish in color; soluble in alcohol; does not concrete as readily as other turpentines.

Fifth.— Chian turpentine is the product of *pistachia terebinthus*, growing in the island of Chio, in the Ægean. It is a thick, greenish yellow liquid.

Essence of turpentine— Oil of turpentine—Spirits of turpentine— Oleum terebinthinæ (U. S., Br.)—is the volatile product of the distillation of turpentine. It is not identical with terebenthene, although that substance is its main constituent; it contains also hydrocarbons isomeric with turpentine and substances containing oxygen, which either pre-exist in the turpentine, or, more usually, result from the method of preparing the oil. When recently distilled, it is a colorless, limpid, neutral liquid; sp. gr. 0.86; usually lævogyrous, sometimes dextrogyrous; when exposed to the air it rapidly becomes yellow and viscid. The action of reagents upon it is practically the same as upon terebenthene.

The number of isomerides existing in oil of turpentine is very great; some are optically active, others inactive; they also vary in their specific gravities, fusing- or boiling-points, and capacity for absorbing oxygen; prominent among them are:

	Specific gravity at 60°.	Fusing-point.	Boiling-point.
Isoterebenthene	0.8116	..	177°
Terebene	0.8266	..	156°
Terebenthene	0.8271	..	156.5°
Camphenes	0.8738	45°	160°

Action on the economy.—Oil of turpentine is used medicinally as a stimulant and diuretic; in large doses it acts as a narcotic-irritant poison. It is eliminated in the form of sulphoconjugated (?) acids with the urine, to which it communicates an odor of violets.

Isomeres of Terebenthene.

Essences.

There exist a great number of bodies, the products of distillation of vegetable substances, which are known as *essences, essential oils, volatile oils, distilled oils*, or *Olea distillata* (U. S.). They resemble each other in being odorous, oily, sparingly soluble in water, more or less soluble in alcohol and ether; colorless or yellowish, inflammable, and prone to become resinous on exposure to air. They are not simple chemical compounds, but mixtures in which some constituent predominates, and in many of them the principal ingredient is a hydrocarbon, isomeric with terebenthene, and consequently having the composition $_nC_{10}H_{16}$; the number of such isomeres is very great. Some contain hydrocarbons, others aldehydes, acetones, phenols, and ethers.

Of the numerous other hydrocarbons closely related to terebenthene, but two require further consideration as being the principal constituents of *caoutchouc* and *gutta-percha*, both of which are isomeric with terebenthene.

Caoutchouc—*India-rubber*—is a peculiar substance existing in suspension in the milky juice of quite a number of trees growing in warm climates. It is, when pure, a mixture of two hydrocarbons—*caoutchene*, $C_{10}H_{16}$, and *isoprene*, C_5H_8.

The commercial article is yellowish brown; sp. gr. 0.919 to 0.942; soft, flexible; almost impermeable, but still capable of acting as a dialyzing membrane when used in sufficiently thin layers. It is insoluble in water and alcohol, both of which, however, it absorbs by long immersion, the former to the extent of twenty-five per cent. and the latter of twenty per cent. of its own weight; it is soluble in ether, carbon disulphide, petroleum, fatty and essential oils; its best solvent is carbon disulphide, either alone, or, better, mixed with five parts of absolute alcohol.

It is not acted upon by dilute mineral acids, but is attacked by concentrated nitric and sulphuric acids, and especially by a mixture of the two. Alkalies tend to render it tougher, although a solution of soda of 40° B. renders it soft after an immersion of a few hours. Chlorine attacks it after a time, depriving it of its elasticity, and rendering it hard and brittle. When heated it becomes viscous at 145°, and fuses at 170°—180° to a thick liquid, which, on cooling, remains sticky and only regains its primitive character after a very long time; on contact with flame it ignites, burning with a reddish and very smoky flame, which is extinguished with difficulty.

The most valuable property of india-rubber, apart from its elasticity, is that which it possesses of entering into combination with sulphur to form what is known as *vulcanized rubber*, which is produced (the details of the process vary) by heating together the normal caoutchouc and sulphur to 130°—150°. Ordinary vulcanized rubber differs materially from the natural gum in its properties; its elasticity and flexibility are much increased; it does not harden when exposed to cold; it only fuses at 200°; finally, it resists the action of reagents, of solvents, and of the atmosphere much better than does the natural gum.

Frequently rubber tubing is too heavily charged with sulphur for certain chemical uses, in which case it may be desulphurized by boiling with dilute caustic soda solution.

Hard rubber, vulcanite, or ebonite, is a hard, tough variety of vulcanized rubber, susceptible of a good polish, and a non-conductor of electricity; used in the manufacture of a great many objects. It contains twenty to thirty-five per cent. of sulphur (the ordinary vulcanized rubber contains seven to ten per cent.), and is prepared by a process which requires great care and experience.

Gutta-percha is the concrete juice of *isonandra gutta.* It is a tough, inelastic, brownish substance, having an odor similar to that of caoutchouc; at ordinary temperatures it is rather hard, but when heated to below the boiling-point of water it becomes soft and may be moulded, or even cast, so as to assume any form, which it retains on cooling; it may be welded with great facility at slightly elevated temperatures, is a good insulating and waterproofing material, and is sufficiently tough and pliable for use for belting for machinery. It is insoluble in water, alkaline solutions, dilute acids, including hydrofluoric, and in fatty oils; it is soluble in benzene, oil of turpentine, essential oils, chloroform, and especially in carbon disulphide. A solution in chloroform is officinal as *Liq. gutta percha* (U. S.), and is used to obtain, by its evaporation, a thin film of gutta percha over parts which it is desired to protect from the air. It is attacked by nitric and sulphuric acids.

When exposed to air and light, it is gradually changed from the surface inward, assuming a sharp acid odor, becoming hard and cracked, and even a conductor of electricity, thus losing, after a time, those characters which render it valuable in the arts.

Gutta-percha is a more complex substance than caoutchouc, and seems to be made up of three substances: *Gutta,* $C_{20}H_{32}$, seventy-five to eighty-two per cent., a white, tough substance, fusing at 150°, soluble in the ordinary solvents of gutta-percha, but insoluble in alcohol and ether. *Albane,* fourteen to nineteen per cent., a white, crystalline resin, heavier than water, fusible at 160°; soluble in benzine, essence of turpentine, carbon disulphide, ether, chloroform, and hot absolute alcohol; not attacked by hydrochloric acid; its composition is $C_{20}H_{32}O_2$. *Fluviale,* four to six per cent., $C_{20}H_{32}O$, a yellowish resin, slightly heavier than water, hard and brittle at 0°, soft at 50°, liquid at 100°; soluble in the solvents of gutta-percha.

Camphors and Resins.

Most of the essential oils yield on distillation two products of different boiling-points; one of these is a hydrocarbon, in most instances of the terebenthene series, liquid at ordinary temperatures, and sometimes known as an *eleoptene.* The other, of higher boiling-point, and solid at ordinary temperatures, designated a *stearoptene,* is an oxidized product, and either exists as such in the vegetable exudation, or is produced during subsequent treatment.

Camphors.

These stearoptenes are probably aldehydes or alcohols corresponding to hydrocarbons related to terebenthene; their composition is clearly determined, although their constitution is as yet uncertain.

They are quite numerous, and many of the varieties occur in several different modifications; the most important are:

Common Camphor — *Japan camphor* — *Laurel camphor* — *Cam-*

pholic aldehyde—*Camphora* (U. S., Br.)—$C_{10}H_{16}O$.—There exist at least three modifications of this substance, which differ from each other, apparently, only in the sources whence they are obtained and in their action upon polarized light; they are:

First.—*Dextrocamphor*, or laurel camphor, obtained from *laurus camphora* = *Camphore officinarum*—$[a]_D = +47.4°$.

Second.—*Lævocamphor*, obtained from *matricaria postlanium*—$[a]_D = -47.4°$.

Third.—*Inactive camphor*, obtained from the essential oils of rosemary, sage, lavender, and origanum, is without action upon polarized light.

The only one of these which is of practical importance is the first, which is the ordinary camphor of the shops.

It occurs as a white, translucent, crystalline solid; sp. gr. 0.986—0.996; of a hot, bitter taste, and a well-known aromatic odor, sparingly soluble in water, to which it communicates its odor. When a small piece is thrown upon water, it takes on a rapid, gyratory motion over the surface, which is instantly stopped when a drop of essential oil is allowed to fall on the water. It is quite soluble in ether, acetic acid, methyl alcohol, carbon disulphide, the oils, and alcohol. The *spir. camphoræ* is an alcoholic solution of two ounces to the pint. It fuses at 175° and boils at 204°. It is volatile at all temperatures, and is readily sublimed.

It ignites readily, and burns with a luminous flame. Cold nitric acid dissolves it, and from the solution it is precipitated unchanged by water. Boiling nitric acid or potassium permanganate solution oxidize it to *dextrocamphoric acid*, $C_{10}H_{16}O_4$. Concentrated sulphuric acid forms with it a black solution, from which water precipitates an oily material called *camphrene*. Distilled with phosphoric anhydride, it yields *cymene*, $C_{10}H_{14}$. Alkaline solutions, by long heating under pressure, convert it into *camphic acid*, $C_{10}H_{16}O_2$, and *borneol*. Chlorine attacks it with difficulty. Bromine unites with it to form an unstable compound, which forms ruby-red crystals having the composition $C_{10}H_{66}OBr_2$. These crystals, when heated to 80°—90°, fuse and give off hydrobromic acid, there remaining an amber-colored liquid, which solidifies on cooling and yields, by recrystallization from boiling alcohol, long, hard, rectangular prisms, insoluble in water, soluble in alcohol, ether, chloroform, and oils; this is the *monobromo-camphor*, recently introduced as a therapeutic agent. When the vapor of camphor is passed over a mixture of fused potash and lime heated to 300°—400°, it unites directly with the potash to form the potassium salt of *campholic acid*, $C_{10}H_{18}O_2$.

Camphor is largely used in the household as a destroyer of moths, and in medicine as an antispasmodic; in overdoses it acts as a poison, the cases, however, usually terminating in recovery. It is said to be a valuable antidote in strychnine-poisoning.

Borneol—*Borneo camphor*—*Camphol*—*Camphyl alcohol*—$C_{10}H_{18}O$—is usually obtained from *dryobalanops camphora*, although it may be obtained from other plants, and even artificially by the hydrogenation of laurel camphor. The product from these different sources is the same chemically, so far as we can determine, but varies, like the modifications of camphor, in its action on polarized light; thus the specific rotary power is of

Borneol from amber,	$[a]_D = +4.1°$
Borneol from dryobalanops,	$[a]_D = +33.4°$
Borneol from madder,	$[a]_D = -33.4°$
Borneol artificial,	$[a]_D = +44.9°$

It forms small, white, transparent, friable crystals; has an odor which recalls at the same time those of laurel camphor and of pepper; has a hot taste; is insoluble in water, readily soluble in alcohol, ether, and acetic acid; fuses at 198°, boils at 212°.

It is a true alcohol, and enters into double decomposition with acids to form ethers. When heated with phosphoric anhydride, it yields a hydrocarbon, *borneene*, $C_{10}H_{16}$. Oxidized by nitric acid, it is converted into laurel camphor.

This substance is very rarely exported from the countries in which it is produced.

Menthol—*Menthyl alcohol*—$C_{10}H_{20}O$—is a camphor existing in essential oil of peppermint. It crystallizes in colorless prisms; fusible at 36°; boiling at 210°; sparingly soluble in water; readily soluble in alcohol, ether, carbon disulphide, and in acids. Corresponding to it are a series of *menthyl* ethers.

Eucalyptol, $C_{12}H_{20}O$—is contained in the leaves of *eucalyptus globulus;* it is liquid at ordinary temperatures, and boils at 175°; by distillation with phosphoric anhydride it yields *eucalyptene*, $C_{12}H_{18}$.

Terpine—*Terebenthene bihydrate*—$C_{10}H_{16},2H_2O+Aq$—is sometimes spontaneously deposited from oil of turpentine containing water; it may be obtained by frequently agitating for a month or more a mixture of oil of turpentine, alcohol, and ordinary nitric acid. It forms fine, large, rhombic prisms; sp. gr. 1.0994; sparingly soluble in cold water; soluble in hot water, alcohol, and ether; fusible at 103°.

Terpinol, $(C_{10}H_{16})_2H_2O$—is formed when terpine in solution in warm water is treated with a very small quantity of sulphuric or of hydrochloric acid, and distilling. It is a colorless liquid; has an odor of hyacinth; sp. gr. 0.852; boils at 168°, at which temperature it suffers partial decomposition. It appears to possess the function of an ether.

Resins.

Notwithstanding the wide diffusion and industrial importance of these substances, and owing to the uncertainty still existing as to their chemical nature, it is difficult to define precisely what is meant by a resin.

They are generally the products of oxidation of the hydrocarbons allied to terebenthene; are amorphous (rarely crystalline); insoluble in water; soluble in alcohol, ether, and essences. Many of them contain acids.

They may be divided into several groups, according to the nature of their constituents: 1st, *Balsams*, which are usually soft or liquid, and are distinguished by containing free *cinnamic* or *benzoic acid* (*q. v.*). The principal members of this group are *benzoin*, *liquidambar*, *Peru balsam*, *styrax*, and *balsam tolu*. 2d. *Oleo-resins* consist of a true resin mixed with an oil, and usually with an oxidized product other than cinnamic or benzoic acid. The principal members of this group are *Burgundy* and *Canada pitch*, *Mecca balsam*, and the resins of *capsicum*, *copaiva*, *cubebs*, *elemi*, *labdanum*, and *lupulin*. 3d. *Gum-resins* are mixtures of true resins and gums. Many of them are possessed of medicinal qualities, *aloes*, *ammoniac*, *asafœtida*, *bdellium*, *euphorbium*, *galbanum*, *gamboge*, *guaiac*, *myrrh*, *olibanum*, *opoponax*, and *scammony*. 4th. *True resins* are hard substances obtainable from the members of the three previous classes, and containing neither essences, gums, nor aromatic acids. Such are *colophony* or *rosin*, *copal*, *dammar*, *dragon's blood*, *jalap*, *lac*, *mastic*, and *sandarac*. 5th. *Fossil resins*, such as *amber*, *asphalt*, and *ozocerite*.

HEXATOMIC ALCOHOLS.

There exist, so far as at present known, but two alcohols of this series, isomeres of each other. They may be regarded as the hydrates of a hydrocarbon of the terebenthene series, C_6H_8, which is only known in combination. They are *mannite* and *dulcite*.

Mannite—*Fraxine—Mannityl hydrate—Mannitic alcohol*—$C_6H_8(OH)_6$—was first obtained from *manna*, of which it forms sixty to eighty per cent. It exists also in a great number of vegetables, and in cider and wine, being formed as one of the products of viscous fermentation. It has also been obtained by partial synthesis, by the action of nascent hydrogen on inverted cane- and milk-sugar. It is best prepared from manna by extraction with boiling alcohol, recrystallization, and decolorization if necessary.

It crystallizes in silky prisms, usually arranged in radiating bundles. It is sweetish in taste; fermentable with difficulty; without action on polarized light; soluble in water and alcohol; insoluble in ether; fusible at 160°; it boils at 200°.

When heated to 100° with hydrochloric acid for some time, it is converted into *mannitan*, $C_6H_{12}O_6$. With the acids generally it combines, with elimination of water, to form mannitic ethers; it also dissolves in alkaline solutions. It is not capable of reducing the cupropotassic solutions, either hot or cold. Nitric acid oxidizes it to *saccharic acid* (*q. v.*), and ultimately to oxalic acid. By the action of moist platinum-black a portion is converted into *mannitic acid*, $C_6H_{12}O_7$, and a portion into *mannitose*, $C_6H_{12}O_6$.

Dulcite—*Melampyrine—Dulcose*—$C_6H_{14}O_6$—the isomere of mannite, is obtained from a Madagascar plant of the genus *melampyrum*. It resembles mannite closely in its properties and reactions, but differs from it in fusing at 182°, and in yielding, when oxidized by nitric acid, mucic in place of saccharic acid.

Saccharic acid, $C_4H_4(OH)_4(COOH)_2$—is a dibasic acid produced by the oxidation of mannite, cane-sugar, and other kinds of sugar. It forms a non-crystalline, friable mass; deliquescent; soluble in water and alcohol; insoluble in ether; it is dextrogyrous when made from cane-sugar. It forms a series of salts and ethers called saccharates.

Mucic acid, $C_6H_{10}O_8$—is a dibasic acid, isomeric with saccharic acid, which it closely resembles. It is formed by the oxidation of dulcite, milk-sugar, or gum arabic, by nitric acid.

It is a white, crystalline powder; very sparingly soluble in cold water, insoluble in alcohol. By long boiling with water it is converted into another isomere, *paramucic acid*, soluble in water and alcohol. Sulphuric acid dissolves it, the solution being red and containing a sulphoconjugate acid. Nitric acid by prolonged action oxidizes it to racemic and oxalic acids. When subjected to dry distillation it is decomposed into water, carbon dioxide, and *pyromucic acid*, $C_5H_4O_3$.

Corresponding to pyromucic acid is an aldehyde, called *furfurol*, or *oil of bran*, a colorless, highly aromatic oil, sp. gr. 1.17; boiling-point, 162°; prepared by distilling bran, starch, sawdust, etc., with dilute sulphuric acid.

CARBOHYDRATES.

The substances classed under this head are composed of carbon, hydrogen, and oxygen; they all contain six atoms of carbon or some multiple of that number, and the hydrogen and oxygen which they contain are always in the same proportion to each other as that in which they exist in water. Their precise constitution is, as yet, not definitely settled, although there are very strong grounds for believing that they are all derivatives of hexatomic alcohols, and that they are, some of them aldehyds, others alcohols, and others ethers. Most of them are important constituents of animal or vegetable organisms, and but few of them have been hitherto produced artificially—none, so far as we know, by complete synthesis.

They are divisible into three well-marked groups, the members of each of which are isomeric with each other, and have many important characters in common. These groups are the following:

I. Glucoses.	II. Saccharoses.	III. Amyloses.
$_n(C_6H_{12}O_6)$.	$_n(C_{12}H_{22}O_{11})$.	$_n(C_6H_{10}O_5)$.
+Glucose.	+Saccharose.	+Starch.
(Dextrose.)	+Lactose.	+Glycogen.
—Lævulose.	+Maltose.	+Dextrin.
Mannitose.	+Melitose.	—Inulin.
+Galactose.	+Melezitose.	Tunicin.
Inosite.	+Trehalose.	Cellulose.
—Sorbin.	+Mycose.	Gums.
—Eucalin.	Synanthrose.	
	+Parasaccharose.	

Glucoses, $C_6H_{12}O_6$.

Glucose—*Grape-sugar—Dextrose—Liver-sugar—Diabetic sugar.*—The substance from which this group takes its name is widely diffused in nature. It exists, accompanied by lævulose, or saccharose, in all sweet and acidulous fruits; in many vegetable juices; in honey; in the animal economy in the contents of the intestines, in the liver, bile, thymus, heart, lungs, blood, and in small quantity in the urine. Pathologically it is found in the saliva, perspiration, fæces, and enormously increased in the blood and urine in diabetes mellitus (see below). It may also be obtained by decomposition of certain vegetable substances called *glucosides* (*q. v.*).

It can be, and is, in the arts, prepared artificially by heating starch or cellulose for twenty-four to thirty-six hours with a dilute mineral acid (sulphuric). Glucose obtained by this method is very largely used, both legitimately and fraudulently; it is, however, liable to contamination with traces of arsenic, which it receives from the sulphuric acid. Starch is also converted into glucose by the influence of a peculiar ferment, *diastase*, formed during the germination of grain.

Glucose crystallizes with difficulty from its aqueous solution in white, opaque, spheroidal masses containing 1 aq.; from alcohol in fine, transparent, anhydrous prisms; at about 60 degrees in dry air the hydrated

glucose loses its water. It is soluble in all proportions in hot water; in one-third part of cold water (less soluble than cane-sugar); soluble in alcohol. It is less sweet in taste than cane-sugar, two and one-half parts of glucose being required to produce the same sweetening as one part of saccharose. Solutions of glucose are dextrogyrous $[\alpha]_D = +57.6°$. When heated to 170° it loses water, and is converted into *glucosan*, $C_6H_{10}O_5$.

When heated with the diluted mineral acids, glucose is decomposed, yielding a brown substance, *ulmic acid*, and, in the presence of air, formic acid. It dissolves in concentrated sulphuric acid without coloration, forming *sulphoglucic acid*. Cold, concentrated nitric acid converts it into *nitro-glucose;* hot dilute nitric acid oxidizes and decomposes it to a mixture of oxalic and oxysaccharic acids. With the organic acids it forms a number of ethers.

Solutions of glucose dissolve potash, soda, lime, baryta, and the oxides of lead and copper, with which it forms well-defined compounds, which are, however, very prone to decomposition. When glucose solution is heated with an alkali, it turns brown (yellow if the quantity of glucose be small), and assumes a peculiar, molasses-like odor; this change is due to the formation of *melassic* and *glucic* acids (see below).

Glucose precipitates silver from solutions of its salts, and in the presence of free ammonia the metal adheres to the sides of the glass vessel as a brilliant mirror. When an alkaline solution of a cupric salt is heated in the presence of glucose, the sugar reduces the copper salt and precipitates cuprous oxide (see below). Mercury is precipitated from an alkaline solution of mercuric cyanide, when heated with glucose. It forms definite, crystalline compounds with sodium chloride. Sodium amalgam converts glucose in aqueous solution into mannite. Subnitrate of bismuth, suspended in a hot solution of glucose, containing sodium carbonate, turns black or brown from its reduction to bismuth. In the presence of yeast it is converted into alcohol and carbon dioxide, by fermentation (see pp. 170, 303); in the presence of sour milk or of cheese, it enters into lactic fermentation.

If a solution of glucose be rendered faintly blue with indigo solution, then faintly alkaline with sodium carbonate solution, and heated to near boiling without agitation, the color changes to violet and then to yellow. The blue color is restored by agitation.

Physiological.—The greater part of the glucose in the economy in health is introduced with the food, either in its own form or as other carbohydrates, which by digestion are converted into glucose; a certain quantity is also produced in the liver at the expense of glycogen, a formation which continues for some time after death. In some forms of diabetes the production of glucose in the liver is undoubtedly greatly increased. The quantity of sugar normally exsisting in the blood varies from 0.81 to 1.231 part per thousand; in diabetes it rises as high as 5.8 parts per thousand.

Under normal conditions and with food not too rich in starch and saccharine materials, the quantity of sugar eliminated as such is exceedingly small—so small indeed that some observers have contested the fact of any being eliminated in health. It is oxidized in the body, and the ultimate products of such oxidation eliminated as carbon dioxide and water. Whether or no intermediate products are formed, is still uncertain; the probability, however, is that there are. The oxidation of sugar is impeded in diabetes. Where this oxidation, or any of its steps, occurs, is at present a matter of conjecture merely; if, as is usually believed,

glucose disappears to a marked extent in the passage of the blood through the lungs, the fact is a strong support of the view that its transformation into carbon dioxide and water does not occur as a simple oxidation, as the notion that sugar or any other substance is "burned" in the lung, beyond the small amount required by the nutrition of the organ itself, is scarcely tenable at the present day.

So long as the quantity of glucose in the blood remains at or below the normal percentage, it is not eliminated in the urine in quantities appreciable by the tests usually employed; when, however, the amount of glucose in the blood surpasses this limit from any cause, the urine becomes saccharine, and that to an extent proportional to the increase of glucose in the circulating fluids. The causes which may bring about such an increase are numerous and varied; many of them are entirely consistent with health, and the mere presence of increased quantities of sugar in the urine is no proof, taken by itself, of the existence of diabetes. Sugar is detectable by the ordinary tests in the urine under the following circumstances: *Physiologically.*—1st, in the urine of pregnant women and during lactation; it appears in the latter stages of gestation and does not disappear entirely until the suppression of the lacteal secretion. 2d, in small quantities in sucking children from eight days to two and one-half months. 3d, in the urine of old persons (seventy to eighty years). 4th, in those whose food contains a large amount of starchy or saccharine material; to this cause is due the apparent prevalence of diabetes in certain localities, as in districts where the different varieties of sugar are produced. *Pathologically.*—1st, in abnormally stout persons, especially in old persons and in women at the period of the menopause; the quantity does not exceed eight to twelve grams per 1,000 c.c., and disappears when starchy and saccharine food is withheld; this form of glycosuria is very liable to develop into true diabetes when it appears in young persons. 2d, in diseases attended with an interference with the respiratory processes—lung diseases, etc. 3d, in diseases in which there is interference with the hepatic circulation—hepatic congestion, compression of the portal vein by biliary calculi, cirrhosis, atrophy, fatty degeneration, etc. 4th, in many cerebral and cerebro-spinal disturbances—general paresis, dementia, epilepsy; by puncture of the fourth ventricle. 5th, in intermittent and typhus fevers. 6th, by the action of many poisons—carbon monoxide, arsenic, chloroform, curari; by injection into an artery of ether, ammonia, phosphoric acid, sodium chloride, amyl nitrite, glycogen. 7th, in true diabetes the elimination of sugar in the urine is constant, unless arrested by suitable regulation of diet, and not temporary, as in the conditions previously mentioned. The quantity of urine is increased, sometimes enormously, and it is of high specific gravity. The elimination of urea is increased absolutely, although the quantity in 1,000 c.c. may be less than that normally existing in that bulk of urine. The quantity of sugar in diabetic urine is sometimes enormous; an elimination of 200 grams in twenty-four hours is by no means uncommon; instances in which the amount has reached 400 to 600 grams are recorded, and one case in which no less than 1,376 grams were discharged in one day. The elimination is not the same at all hours of the day; during the night less sugar is voided than during the day; the hourly elimination increases after meals, reaching its maximum in four hours, after which it diminishes to reach the minimum in six to seven hours, when it may disappear entirely; this variation is more pronounced the more copious the meal. It is obvious from the above, that, in order that quantitative determinations of sugar in

urine shall be of clinical value, it is necessary that the determination be made in a sample taken from the mixed urine of twenty-four hours.

The relation existing between the quantity of sugar in the blood and its elimination by the urine in diabetes is well shown by the following results of Pavy, which also show the beneficial effects of restricting the diet:

	Urine.				Blood.
	Quantity in 24 hours.	Specific gravity.	Sugar excreted in 24 hours.	Sugar in 1,000 parts.	Sugar in 1,000 parts.
Case I. Mixed diet	6608 c.c.	1040	751.6 grams.	109.91	5.763
Case II. Mixed diet	6474 c.c.	1041	633.0 grams.	94.08	5.545
Case II. Restricted diet	3407 c.c.	1031	245.2 grams.	61.34	2.625
Case III. Mixed diet	5878 c.c.	1036	567.7 grams.	93.39	4.970
Case III. Restricted diet	2470 c.c.	1033	115.8 grams.	45.49	2.789
Case IV. Partly restricted diet	1704 c.c.	1036	21.81 grams.	48.11	1.848
Case IV. Partly restricted diet, 3½ months later	852 c.c.	1034	14.40 grams.	31.76	1.543

Tests for the presence of glucose.—A saccharine urine is usually abundant in quantity, pale in color, of high specific gravity, covered with a persistent froth on being shaken, and exhales a peculiar odor; when evaporated it leaves a sticky residue. The presence of glucose in urine is indicated by the following tests:

If the urine be albuminous, it is indispensable that the albumen be separated before any of the tests for sugar are applied; this is done by adding one or two drops of acetic acid, or, if the urine be alkaline, just enough acetic acid to turn the reaction to acid, *and no more*, heating over the water-bath until the albumen has separated in flocks, and filtering.

First.—When examined by the polarimeter (see p. 303) it deviates the plane of polarization to the right.

Second.—When mixed with an equal volume of liquor potassæ and heated, it turns yellow, and, if sugar be abundant, brown; a molasses-like odor is at the same time observable (Moore's test).

Third.—The urine, rendered faintly blue with indigo solution and faintly alkaline with sodium carbonate, and heated to boiling without agitation, turns violet and then yellow if sugar be present; on agitation the blue color is restored (Mulder-Neubauer test).

Fourth.—About 1 c.c. of the urine, diluted with twice its bulk of water, is treated with two or three drops of cupric sulphate solution and about 1 c.c. of caustic potassa solution; if sugar be present the bluish precipitate is dissolved on agitation, forming a blue solution; the clear blue fluid, when heated to near boiling, deposits a yellow, orange, or red precipitate of cuprous oxide if sugar be present (Trommer's test). In the application of this test an excess of cupric sulphate is to be avoided, lest the color be masked by the formation of the black cupric oxide. Sometimes no precipitate is formed, but the liquid changes in color from blue to yellow; this occurs in the presence of small quantities of cupric salt and large quantities of sugar, the cuprous oxide being held in solution by the excess of glucose; in this case the test is to be repeated, using a sample of urine more diluted with water. In some instances, also, the reaction is interfered with by excess of normal constituents of the urine, uric acid, creatinine, coloring matter, etc., and, instead of a bright precipitate, a

muddy deposit is formed; when this occurs the urine is heated with animal charcoal, and filtered; the filtrate evaporated to dryness; the residue extracted with alcohol; the alcoholic extract evaporated; the residue redissolved in water, and tested as described above.

Fifth.—Four or five cubic centimetres of Fehling's solution (see p. 304) are heated in a test-tube to boiling; it should remain unaltered; the urine is then added guttatim; if it contain sugar, the mixture turns green and a yellow or red precipitate of cuprous oxide is formed, usually darker in color than that obtained by Trommer's test. The absence of glucose is not to be inferred until a bulk of urine equal to that of the Fehling's solution used has been added, and, the mixture boiled from time to time without the formation of a precipitate. This test is certainly the most convenient and the most reliable for clinical purposes.

Sixth.—A few cubic centimetres of the urine are mixed in a test-tube with an equal volume of solution of sodium carbonate (one part crystal. carbonate and three parts water), a few granules of bismuth subnitrate are added, and the mixture boiled for some time (until it begins to "bump," if necessary); if sugar be present, the bismuth powder turns brown or black by reduction to elementary bismuth (Boettger's test). No other normal constituent of the urine reacts with this test; a fallacy is, however, possible from the presence of some compound, which, by giving up sulphur, may cause the formation of the black bismuth sulphide; to guard against this, when an affirmative result has been obtained, another sample of urine is rendered alkaline with caustic potassa solution and boiled with pulverized litharge; the powder should not turn black.

Use may also be made in this test of an alkaline solution of bismuth, made by dissolving four grams of Rochelle salts in 100 grams of caustic potassa solution of sp. gr. 1.33, warming gently, and adding bismuth subnitrate as long as it dissolves (about two grams). A few drops of this solution are added to three or four cubic centimetres of the urine, which is then boiled. The reagent does not keep well.

Seventh.—A solution of sugar, mixed with good yeast and kept at 25°, is decomposed into carbon dioxide and water. To apply the fermentation-test to urine, take three test-tubes, A, B, and C, place in each some washed (or compressed) yeast, fill A completely with the urine to be tested, and place it in an inverted position, the mouth below the surface of some of the same urine in another vessel (the entrance of air being prevented, during the inversion, by closing the opening of the tube with the finger, or a cork on the end of a wire, until it has been brought below the surface of the urine). Fill B completely with some urine to which glucose has been added, and C with distilled water, and invert them in the same way as A: B in saccharine urine, and C in distilled water. Leave all three tubes in a place where the temperature is about 25°, for twelve hours, and then examine them. If gas have collected in B over the surface of the liquid, and none in A, the urine is free from sugar; if gas has collected in both A and B, and not in C, the urine contains sugar; if no gas has collected in B, the yeast is worthless, and if any gas be found in C, the yeast itself has given off CO_2; in the last two cases the process must be repeated with a new sample of yeast.

Quantitative determination of glucose.—First.—By the polarimeter.—The filtered urine is observed by the polariscope (see p. 31) and the mean of half a dozen readings taken as the angle of deviation; from this the percentage of sugar is determined by the formula $p = \frac{a}{57.6 \times l}$, in which

p=the weight, in grams, of glucose in 1 c.c. of urine; a=the angle of deviation; l=the length of the tube in decimeters. The same formula may be used for other substances by substituting for 57.6 the value of $[a]_D$ for that substance.

If the urine contain albumen, it must be removed, as it exerts an action on polarized light opposite to that of glucose. It is always preferable, if possible, to observe the urine without treatment for decolorization; if, however, it be too highly colored, some treatment becomes necessary. The use of animal charcoal for this purpose should be avoided, as it retains a considerable quantity of sugar; the best method is to add a known volume of lead subacetate and filter, account being taken in the calculation of the dilution so caused.

Second.—By specific gravity; Robert's method.—The specific gravity of the urine is carefully determined at 25°; yeast is then added, and the mixture kept at 25° until fermentation is complete; the specific gravity is again observed, and will be found to be lower then before; each degree of diminution represents 0.2196 grams of sugar in 100 c.c. of urine.

Neither *first* nor *second* gives strictly accurate results, even when carefully conducted; the results are, however, sufficiently accurate for medical purposes.

Third.—By Fehling's solution.—Of the many formulæ for Fehling's solutions, the one to which we give the preference is that of Dr. Piffard. Two solutions are required:

I.	Cupric sulphate (pure, crystals).....	51.98 grams.
	Water	500.0 c.c.
II.	Rochelle salt (pure, crystals).....	259.9 grams.
	Sodic hydrate solution, sp. gr. 1.12.....	1000.0 c.c.

When required for use, one volume of No. I. is mixed with two volumes of No. II. The copper contained in 20 c.c. of this mixture is precipitated as cuprous oxide by 0.1 gram glucose.

To use the solution, 20 c.c. of the mixed solutions are placed in a flask of 250—300 c.c. capacity, 40 c.c. of distilled water are added, the whole thoroughly mixed and heated to boiling. On the other hand, the urine to be tested is diluted with four times its volume, if poor in sugar, and with nine times its volume if highly saccharine (the degree of dilution required is, with a little practice, readily determined by the appearance of the deposit obtained in the qualitative testing); the water and urine are thoroughly mixed and a burette filled with the mixture. A few drops of aqua ammoniæ are added to the Fehling's solution and the diluted urine added, in small portions toward the end, until the blue color is entirely discharged—the contents of the flask being made to boil briskly between each addition from the burette. When the liquid in the flask shows no blue color when looked through with a white background, the reading of the burette is taken; this reading, divided by five if the urine was diluted with four volumes of water, or by ten if with nine volumes, gives the number of cubic centimetres of urine containing 0.1 gram of glucose; and consequently the elimination of glucose in twenty-four hours, in decigrams, is obtained by dividing the number of cubic centimetres of urine in twenty-four hours by the result obtained above.

Example.—20 c.c. Fehling's solution used, and urine diluted with four volumes of water.

Reading of burette: 36.5 c.c. $\frac{36.5}{5} = 7.3$ c.c. urine contain 0.1 gram glucose. Patient is passing 2,436 c.c. urine in twenty-four hours. $\frac{2,436}{7.3} = 333.6$ decigr. $= 33.36$ gram glucose in twenty-four hours.

The accuracy of the determination may be controlled by filtering off some of the fluid from the flask at the end of the reaction; a portion of the filtrate is acidulated with acetic acid and treated with potassium ferrocyanide solution; if it turn reddish brown, the reduction has not been complete, and the result is affected with a plus error. To another portion of the filtrate a few drops of cupric sulphate solution are added and the mixture boiled; if any precipitation of cuprous oxide be observed, an excess of urine has been added, and the result obtained is less than the true one.

This method, when carefully conducted with accurately prepared and undeteriorated solutions, is the best adapted to clinical uses. The copper solution should be kept in the dark, in a well-closed bottle, and the stopper and neck of the No. II. solution should be well coated with paraffin.

Fourth.—Gravimetric method.—When more accurate results than are obtainable by Fehling's volumetric process are desired, recourse must be had to a determination of the weight of cuprous oxide obtained by reduction. A small quantity of freshly prepared Fehling's solution is heated to boiling in a small flask; to it is gradually added, with the precautions observed in the volumetric method, a known volume of urine, such that at the end of the reduction there shall remain an excess of unreduced copper salt. The flask is now completely filled with boiling water, corked, and allowed to cool. The alkaline fluid is separated as rapidly as possible from the precipitated oxide by decantation and filtration through a small double filter, and the precipitate and flask repeatedly washed with hot water until the washings are no longer alkaline; a small portion of the precipitate remains adhering to the walls of the flask. The filter and its contents are dried and burned in a weighed porcelain crucible; when this has cooled, the flask is rinsed out with a small quantity of nitric acid; this is added to the contents of the crucible, evaporated over the water-bath, the crucible slowly heated to redness, cooled, and weighed; the difference between this last weight and that of the crucible + that of the filter-ash, is the weight of cupric oxide, of which 220 parts=100 parts of glucose.

Lævulose—*Uncrystallizable sugar*—forms the uncrystallizable portion of the sugar of fruits and of honey, in which it is associated with glucose; it is also produced artificially by the prolonged action of boiling water upon *inulin*, and as one of the constituents of inverted sugar (see p. 308). It may be separated from inverted sugar by adding calcic hydrate, expressing the soluble calcium-glucose compound, suspending the sparingly soluble lævulose-calcium compound in water, decomposing with oxalic acid, and evaporating the solution.

Lævulose is not capable of crystallization, but may be obtained as a thick syrup; very deliquescent and soluble in water, insoluble in absolute alcohol; it is sweeter but less readily fermentable than glucose, which it equals in the readiness with which it reduces cupro-potassic solutions. Its prominent physical property, and that to which it owes its name, is

its strong left-handed polarization, $[a]_D = -106°$ at 15°. When heated to 170°, it is converted into the solid, amorphous *lævulosan*, $C_6H_{10}O_5$.

Mannitose is obtained by the oxidation of mannite, whose aldehyde it probably is. It is a yellow, uncrystallizable sugar, having many of the characters of glucose, but being optically inactive.

Galactose—sometimes improperly called lactose—is formed by the action of dilute acids upon lactose, milk-sugar, as glucose is formed from saccharose. It differs from glucose in crystallizing more readily, in being very sparingly soluble in cold alcohol, in its action upon polarized light, $[a]_D = +83.33°$, and in being oxidized to mucic acid by nitric acid.

Inosite—*Muscle-sugar*—exists in the liquid of muscular tissue, in the lungs, kidneys, liver, spleen, brain, and blood; pathologically, in the urine in Bright's, diabetes, and after the use of drastics in uræmia, and in the contents of hydatid cysts; also in the seeds and leaves of certain plants. What the source and function of inosite in the animal economy may be is still a matter of conjecture.

It may be prepared from muscular tissue or from green beans; the latter are reduced to a pulp, boiled with water for half an hour, expressed, the liquid reduced to a syrup over the water-bath, treated with alcohol until a persistent deposit is formed, and set aside; crystalline crusts of inosite separate.

It forms long, colorless, monoclinic crystals, containing two molecules of water of crystallization, usually arranged in groups having a cauliflower-like appearance. It effloresces in dry air; has a distinctly sweet taste; is easily soluble in water, difficultly in alcohol; insoluble in absolute alcohol and in ether; it is without action upon polarized light.

The position of inosite in this series is based entirely upon its chemical composition, as it does not possess the other characteristics of the group. It does not enter directly into alcoholic fermentation, although upon contact with putrefying animal matters it produces lactic and butyric acids; when boiled with barium or potassium hydrate, it is not even colored; in the presence of inosite, potash precipitates with cupric sulphate solution, the precipitate being redissolved in an excess of potash; but no reduction takes place upon boiling the blue solution.

The presence of inosite is indicated by the following reactions: *Scherer's.*—Treated with nitric acid, the solution evaporated to near dryness, and the residue moistened with ammonium hydrate and calcium chloride, and again evaporated; a rose-pink color is produced. Succeeds only with nearly pure inosite. *Gallois'.*—Mercuric nitrate produces, in solutions of inosite, a yellow precipitate which, on cautious heating, turns red; the color disappears on cooling, and reappears on heating.

Sorbin—obtained from the fermented juice of berries of the mountain ash, in which it is formed by the decomposition of malic acid. It forms colorless crystals, sweet, hard, and transparent; very soluble in water; very sparingly soluble in hot alcohol; its solutions are lævogyrous, $[a]_D = -35.97°$; are not fermentable, but reduce Fehling's solution.

Eucalin—formed by the fermentation of melitose; it appears as a faintly sweet, syrupy liquid; dextrogyrous, $[a]_D = +50°$ about; it reduces cupro-potassic solutions, and is oxidized by nitric acid to oxalic acid.

Saccharoses, $C_{12}H_{22}O_{11}$.

Saccharose—*Cane-sugar—Beet-sugar*—is by far the most important member of the group; it has been known from early antiquity, and is very abundant in vegetable nature; it exists in many roots, fruits, and grasses, and is produced principally, not to say exclusively, from the sugar-cane, *saccharum officinarum*, sorghum, *sorghum saccharatum*, beet, *beta vulgaris*, and sugar-maple, *acer saccharinum*.

For the extraction of sugar from the canes, these are crushed, the expressed juice is drawn off into large pans, in which it is heated to about 100°; milk of lime is now added, which causes the precipitation of impurities, albumen, wax, calcic phosphate, etc.; the clear liquid is drawn off, and "delimed" by passing a current of carbon dioxide through it; the clear liquid is again drawn off and evaporated, during agitation, to the crystallizing-point; the product is drained, leaving what is termed "raw" or "muscovado" sugar, while the liquid which drains off is molasses, *Syrupus fuscus* (U. S.). The sugar so obtained is unfit for human consumption, and is purified by the process of "refining," which consists essentially in adding to the raw sugar, in solution, albumen in some form, filtering first through canvas, afterward through animal charcoal; the clear liquid is evaporated in "vacuum-pans" at a temperature not exceeding 72°, to the crystallizing-point; the product is allowed to crystallize in earthen moulds, a saturated solution of pure sugar is poured upon the crystalline mass in order to displace the uncrystallizable sugar which still remains, and the loaf is finally dried in an oven. The liquid displaced as above is what is known as "sugar-house syrup," a product which is now, however, largely and fraudulently produced from artificial glucose.

Pure sugar should be entirely soluble in water; the solution should not turn brown when warmed with dilute potassium hydrate solution; should not reduce Fehling's solution; and should give no precipitate with ammonium oxalate.

Beet-sugar is the same as cane-sugar, except that, as usually met with in commerce, it is lighter, bulk for bulk. "Sugar-candy," or "rock-candy," is cane-sugar allowed to crystallize slowly from a concentrated solution without agitation. Maple-sugar is a partially refined, but not decolorized variety of cane-sugar.

Saccharose crystallizes, as usually seen, in small, white, monoclinic prisms; or as sugar-candy, in large, yellowish, transparent crystals; sp. gr. 1.606. It is very soluble in water, dissolving in about one-third its weight of cold water, and more abundantly in hot water; it is insoluble in absolute alcohol or ether, and its solubility in water is progressively diminished by the addition of alcohol. Aqueous solutions of cane-sugar are dextrogyrous, $[a]_D = +73.8°$.

When saccharose is heated to 160° it fuses, and the liquid, on cooling, solidifies to a yellow, transparent, amorphous mass known as "barley-sugar"; at a slightly higher temperature it is decomposed into glucose and lævulosan; at a still higher temperature, water is given off, and the glucose already formed is converted into glucosan; at 210° the evolution of water is more abundant, and there remains a brown material known as "caramel," or "burnt sugar," a tasteless substance, insoluble in strong alcohol, but soluble in water or aqueous alcohol, and used to communicate color to spirits; finally, at higher temperatures, methyl hydride and the

two oxides of carbon are given off; a brown oil, acetone, acetic acid, and aldehyde distil over, and a carbonaceous residue remains.

If saccharose be boiled for some time with water, it is converted into *inverted sugar*, which is a mixture of glucose and lævulose:

$$\underset{\text{Saccharose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Lævulose.}}{C_6H_{12}O_6}$$

With a solution of saccharose the polarization is dextrogyrous, but, after inversion, it becomes lævogyrous, because the left-handed action of the molecule of lævulose produced, $[a]_D = -106°$, is only partly neutralized by the right-handed action of the glucose, $[a]_D = +57.6°$. This inversion of cane-sugar is utilized in the testing of samples of sugar. On the other hand, it is to avoid its occurrence, and the consequent loss of sugar, that the vacuum-pan is used in refining—its object being to remove the water at a low temperature.

Those acids which are not oxidizing agents act upon saccharose in three ways, according to circumstances: 1st, if tartaric and other organic acids be heated for some time with saccharose to 100°—120°, compounds known as *saccharides*, and having the constitution of ethers, are formed; 2d, heated with mineral acids, even dilute, and less rapidly with some organic acids, saccharose is quickly converted into inverted sugar; 3d, concentrated acids decompose cane-sugar entirely, more rapidly when heated than in the cold; with hydrochloric acid, formic acid and a brown, flocculent material (ulmic acid ?) are formed; with sulphuric acid, sulphur dioxide and water are formed, and a voluminous mass of charcoal remains. Oxalic acid, aided by heat, produces carbon dioxide, formic acid, and a brown substance (humine ?).

Oxidizing agents act energetically upon cane-sugar, which is a good reducing agent. With potassium chlorate, sugar forms a mixture which detonates when subjected to shock, and which deflagrates when moistened with sulphuric acid. Dilute nitric acid, when heated with saccharose, oxidizes it to saccharic and oxalic acids. Concentrated nitric acid, alone or mixed with sulphuric acid, converts it into the explosive *nitro-saccharose*. Potassium permanganate, in acid solution, oxidizes it completely to carbon dioxide and water.

Cane-sugar reduces the compounds of silver, mercury and gold, when heated with their solutions; it does not reduce the cupro-potassic solutions in the cold, but effects their reduction when heated with them to an extent proportional to the amount of excess of alkali present.

When ground up with potash, or moderately heated with liquor potassæ, cane-sugar does not turn brown, as does glucose; but by long ebullition it is decomposed by the alkalies much less readily than glucose, with formation of acids of the fatty series and oxalic acid.

With the bases, saccharose is capable of forming definite compounds called *sucrates* (improperly saccharates, a name belonging to the salts of saccharic acid). With calcium it forms no less than five compounds. Hydrate of calcium dissolves readily in solutions of sugar, with formation of a calcium compound, soluble in water, containing an excess of sugar; a solution containing one hundred parts of sugar in six hundred parts of water dissolves thirty-two parts of calcic oxide. These solutions have an alkaline taste; are decomposed, with formation of a gelatinous precipitate, when heated, and with deposition of calcium carbonate and regeneration of saccharose, when treated with carbon dioxide. Quantities of cal-

cium sucrates are frequently introduced into sugars to increase their weight—an adulteration the less readily detected, as the sucrate dissolves with the sugar. Calcium sucrates exist in the *Liq. calcis saccharatus* (B. P.).

Yeast causes fermentation of solutions of cane-sugar, but only after its conversion into glucose; fermentation is also caused by exposing a solution of sugar containing ammonium phosphate to the air.

During the process of digestion, probably in the small intestine, cane-sugar is converted into glucose.

Lactose—*Milk-sugar—Lactine—Saccharum lactis* (U. S., Br.)—has hitherto been found only in the milk of the mammalia. It may be obtained from skim-milk by coagulating the casein with a small quantity of sulphuric acid, filtering, evaporating, redissolving, decolorizing with animal charcoal, and recrystallizing.

It forms prismatic crystals; sp. gr. 1.53; hard, transparent, faintly sweet, soluble in six parts of cold water and in two and one-half parts of boiling water, soluble in acetic acid, insoluble in alcohol and in ether; its solutions are dextrogyrous, $[a]_D = +59.3°$. The crystals, dried at 100°, contains 1 aq., which they lose at 150°.

Lactose is not altered by contact with air. Heated with dilute mineral or with strong organic acids, it is converted into galactose. Nitric acid oxidizes it to mucic and oxalic acids; a mixture of nitric and sulphuric acids converts it into an explosive nitro-compound. With organic acids it forms ethers. With soda, potash and lime it forms compounds similar to those of saccharose, from which lactose may be recovered by neutralization, unless they have been heated to 100°, at which temperature they are decomposed. If cupric sulphate solution be added to a solution of lactose and afterward potassium hydrate solution, a precipitate is formed which is redissolved in an excess of alkali; the cupric compound in this solution is reduced, on boiling, with precipitation of cuprous oxide. Lactose also reduces Fehling's solution.

In the presence of yeast, lactose is capable of alcoholic fermentation, which takes place slowly and, as it appears, without previous transformation of the lactose into either glucose or galactose. On contact with putrefying albuminoids it enters into lactic fermentation.

The average proportion of lactose in different milks is as follows: Cow, 5.5 per cent.; mare, 5.5; ass, 5.8; human, 5.3; sheep, 4.2; goat, 4.0. When taken internally, it is converted into galactose by the pancreatic secretion; when injected into the blood, it does not appear in the urine, which, however, contains glucose.

Maltose—A sugar closely resembling glucose in many of its properties, and existing in malt, being the first product of the action of diastase upon starch. It crystallizes as does glucose, but differs from that sugar in being less soluble in alcohol and in exerting a dextrogyratory power three times as great.

Melitose is obtained from the sweet exudation formed by various species of Australian *eucalyptus* (Australian manna), from which it may be extracted by solution in water, decolorization by animal charcoal, and crystallization.

It crystallizes in long needles, with 3 aq., of which it loses two at 100°, and the last at 130°; it is very soluble in water, the solutions being sweet, and dextrogyrous, $[a]_D = +102°$.

Dilute acids convert it into glucose and eucalin; it is not colored when boiled with alkalies, nor does it reduce cupro-potassic solutions.

Melezitose is obtained from an exudation of *Larix europæa* (Briançon manna). It forms small, monoclinic prisms, sweet, efflorescent, very soluble in water. Its solutions are dextrogyrous, $[a]_D = 94.1°$, do not reduce cupro-potassic solutions, are not fermentable, and are converted, by boiling with dilute acids, into solutions of glucose.

Trehalose is obtained from a Turkish manna, known as *trehala*. It crystallizes in hard octahedra with 2 aq., which it loses at 100°. It does not reduce Fehling's solution; is not fermentable, is very soluble in water; the solution being dextrogyrous, $[a]_D = +220°$.

Mycose is a sugar existing in ergot. It resembles trehalose in all its properties, except that it does not entirely lose its water of crystallization at 100°, and that it has a lower dextrogyratory action.

Synanthrose exists, accompanied by inuline and glucose in the ripe tubercles of *dahlia*, *helianthus*, etc. It crystallizes with 1 aq.; is not directly fermentable; has no action upon polarized light; is not colored by cold potash solution; and only reduces cupro-potassic solutions after prolonged boiling.

Parasaccharose is an isomeric modification of cane-sugar, produced by the fermentation in summer of solutions of cane-sugar by exposure to air in the presence of ammonium phosphate. It differs from saccharose in its rotary power, $[a]_D = +107°$; and in its power to reduce alkaline solutions of cupric salts.

Amyloses, $_n(C_6H_{10}O_5)$.

Starch—*Amylum*—the most important member of the group, is very widely disseminated in the vegetable kingdom, existing, as it does, in the roots, stems, and seeds of all plants.

It is prepared extensively for use in the arts and as an article of diet from rice, wheat, potatoes, maniot, beans, sago, arrow-root, etc. The process generally followed consists in steeping the comminuted vegetable tissue for a considerable time in water rendered faintly alkaline with soda; the softened mass is then rubbed on a sieve under a current of water, which washes out the starch-granules; the washings are allowed to deposit the starch, which, after washing by decantation, is dried at a low temperature.

Starch is a white powder, having a peculiar slippery feel, but it sometimes appears in short columnar masses. The granules of starch have a similar appearance from whatever source they are obtained, yet those from different kinds of plants differ sufficiently to allow of their distinction by microscopic examination. They are rounded or egg-shaped masses, having in the centre or toward one end a spot, called the *hilum*, around which are a series of concentric lines, indicating the junctions of the various layers of which the granules are composed—these markings varying in character and distinctness in different plants. The main characters of the principal kinds of starch are given in the table on next page.

Starch is not altered by exposure to air, from which, however, it absorbs moisture; commercial dried starch contains eighteen per cent. of moisture, of which it loses eight per cent. in vacuo, and the remaining ten per cent. when heated to 145°. It is insoluble in alcohol, ether, cold acids, and cold water. If fifteen to twenty parts of water be gradually heated with one part of starch, the granules swell at about 55°, and at 80° they have reached thirty times their original dimensions; their struc-

ture is no longer distinguishable, and they form, by their agglutination with each other, a translucent, gelatinous mass, commonly known as starch paste; in this state the starch is said to be hydrated, and, if boiled with much water and the liquid filtered, a solution of starch passes through, which is opalescent from the suspension in it of undissolved particles. Dilute solutions of the alkalies produce the same effects on starch in the cold as does hot water. Hydrated starch is dextrogyrous, $[\alpha]_D = +216°$.

CHARACTERS OF STARCH-GRANULES.

From	Average size in millimetres.	Shape.	Hilum.	Rings.
Tous les mois	.0939—.0469	Oval	Ex.	In. F. R.
Curcuma arrow-root	.0304—.0609	Irreg. oval.	Ex. ft.	In. Cl.
Maranta arrow-root	.01 —.07	Ovoid	Central.	....
Natal arrow-root	.0375—.0327	Ovoid	Ex.	Cl.
Potato	.0376—.0686	Circ. ovate.	Central.	Cl.
Ginger	.0376—	Ovoid	Cl.	....
Galangal	.0342—	Ovoid	Cl.	Ft.
Calumba	.0469—	Pear	Cl.	Ft. C.
Orris-root	.028 —	Elongated.	Ft.	....
Turmeric	.0376—	Oval	Cl.	In. Cl.
Bean	.0343—	Oval	Stellate.	Ft.
Pea	.0177—.0282	Oval	Stellate.	Ft.
Lentil	.0282—	Oval	Linear.	Ft.
Pepper	.005 —.0005	Polygonal.	Central.	....
Nutmeg	.014 —	Pentagonal.	.....	Ft.
Dari	.0188—	Hexagonal.	.....	Ft.
Maize	.0188—	Round	.....	Ft.
Wheat	.0022—.216	Round	Inv.	Inv.
Barley	.0185—.07	Round	Inv.	Inv.
Rye	.0375—.0022	Round	Inv.	Inv.
Chestnut	.0022—.022	Elliptic.	Inv.	Inv.
Acorn	.0188—	Round	Ex.	Inv.
Sago	.0282—.066	Oval	Ex.	Ft.
Tapioca	.0188—.014	Conical.	Ex.	....
Arum arrow-root	.014 —	Truncated.	Ex.	Ft.
Oat	.0094—	Polyhedral.	.....	....
Tahiti arrow-root	.019 —.0094	Truncated.	Stellate.	....
Rice	.0076—.005	Polygonal.	Stellate.	....

Ex.=excentric; In.=incomplete; F.=fine; R.=regular; Ft.=faint; Cl.=clearly defined; C.=complete; Inv.=invisible.

When subjected to dry heat, the granules of starch swell and burst; at 200° it is converted into *dextrin;* at 230° it forms a brownish yellow fused mass, composed principally of *pyrodextrin.* Hydrated starch is converted into dextrin by heating with water at 160°, and, if the action be prolonged, the new product is changed to glucose.

If starch be ground up with dilute sulphuric acid, after about half an hour the mixture gives only a violet color with iodine (see below); if now the acid be neutralized with chalk and the filtered liquid evaporated, it yields a white, granular product, which differs from starch in being soluble in water, especially at 50°, and in having a lower rotary power, $[a]_D = +211°$. If the action be prolonged, the value of $[a]_D$ continues to sink until it reaches +73.7°, when the product consists of a mixture of dextrin and glucose. Concentrated nitric acid dissolves starch in the cold, forming a nitro-product called *xylodin* or *pyroxam*, which is insoluble in water, soluble in a mixture of alcohol and ether; explosive. Hydrochloric and oxalic acids convert starch into glucose. When starch is heated under pressure to 120° with stearic or acetic acid, compounds are formed which seem to be ethers, and to indicate that starch is the hydrate of a trivalent, oxygenated radical, $(C_6H_7O_2)'''$. Tannic acid produces in cold solutions of starch a precipitate, soluble at 50°, and deposited on cooling. Potash and soda in dilute solutions convert starch into the soluble modification mentioned above.

A dilute solution of iodine produces a more or less intense blue-violet color with starch, either dry, hydrated, or in solution, the color disappearing on the application of heat, and returning on cooling; if to a solution of starch, blued by iodine, a solution of a neutral salt be added, there separates a blue, flocculent deposit of the so-called *iodide of starch*. Iodine renders starch soluble in water, and a soluble iodized starch is obtained by triturating together nine parts of starch, two parts water, and one part iodine; the mixture is then heated over the water-bath for two hours, cooled, and precipitated by the addition of the proper quantity of alcohol.

The amount of starch contained in food vegetables varies from about five per cent. in turnips to 89 per cent. in rice, as will be observed in the following table:

COMPOSITION OF VEGETABLE FOODS.

	Nitrogenized matter.	Starch.	Dextrin, etc.	Cellulose.	Fat.	Mineral matter.	Carbohydrate.	Water.	Vegetable fibre, etc.	Authority.
Wheat, hard	22.75	58.62	9.50	3.50	2.61	3.02	...	...	..	Payen.
Wheat, hard	19.50	65.07	7.60	3.0	2.13	2.71	...	...	..	Payen.
Wheat, hard	20.0	63.80	8.0	3.10	2.25	2.85	...	...	..	Payen.
Wheat, semi-hard	15.25	70.05	7.0	3.0	1.95	2.75	...	...	..	Payen.
Wheat, soft	12.65	76.51	6.05	2.80	1.87	2.12	...	...	..	Payen.
Rye	12.50	64.65	14.90	3.10	2.25	2.60	...	...	..	Payen.
Barley	12.96	66.43	10.0	4.75	2.76	3.10	...	...	..	Payen.
Oats	14.39	60.59	9.25	7.06	5.50	3.25	...	...	..	Payen.
Maize	12 50	67.55	4.0	5.90	8.80	1.25	...	...	..	Payen.
Rice	7.55	86.65	1.0	1.10	0.80	0.90	...	...	..	Payen.
Flour	14.45	...	...	..	1.25	1.60	68.48	14.22	..	Payen.
Flour	10.80	...	...	..	2.0	1.70	70.50	15.0	..	Letheby.
Bread	8.10	...	...	..	1.60	2.30	51.00	37.0	..	Letheby.
Oatmeal	12.60	...	...	..	5.60	3.0	63.80	15.0	..	Letheby.
Buckwheat	13.10	64.90	...	3.50	3.0	2.50	...	13.0	..	Payen.
Quinoa seeds	22.86	56.80	...	..	5.74	5.05	...	...	9.53	Voelcker.
Quinoa flour	19.0	60.0	...	..	5.0	..	...	16.0	..	Voelcker.
Horse-bean	30.80	48.30	...	3.0	1.90	3.50	...	12.50	..	Payen.
Broad bean	29.05	55.85	...	1.05	2.0	3.65	...	8.40	..	Payen.
White bean	25.50	55.70	...	2.09	2.80	3.20	...	9.90	..	Payen.
Peas, dried	23.80	58.70	...	3.50	2.10	2.10	...	8.30	..	Payen.
Lentils	25.20	56.0	...	2.40	2.60	2.30	...	11.50	..	Payen.
Potato	2.50	20.0	1.09	1.04	0.11	1.26	...	74.0	..	Payen.
Potato	2.10	18.80	3.20	..	0.20	0.70	...	75 0	..	Letheby.
Sweet potato	1.50	16.05	10.20	0.45	0.30	2.60	...	67.50	1.10	Payen.
Carrots	1.30	8.40	6.10	..	0.20	1.0	...	83.0	..	Letheby.
Parsnip	1.10	9.60	5.80	..	0.50	1.0	...	82.0	..	Letheby.
Turnip	1.20	5.10	2.10	..	..	0.60	...	91.0	..	Letheby.

Starch has not been found in the animal economy outside of the alimentary canal, in which, as a prerequisite to its absorption, it must be converted into dextrin and glucose. This change is partially effected by the action of the saliva, more rapidly with hydrated than with dry starch, and more rapidly with the saliva of some animals than that of others, those of man and of the rabbit acting much more quickly than those of the horse and dog. The greater part of the starch taken with the food passes into the small intestine unchanged; here, under the influence of the pancreatic ferment, the most complete transformation into glucose, and of a portion into lactic and butyric acids, takes place. If, however, the diet is abnormally rich in starch, a portion is wasted, passing out unchanged in the fæces.

Glycogen.—This interesting body, which has been the subject of much discussion, was discovered by Cl. Bernard in the liver, and subsequently in the placenta; it has also been found to exist in white blood-corpuscles, pus-cells, young cartilage-cells, in many embrionic tissues, and in muscular tissue. During the activity of muscles the amount of glycogen which they contain is diminished, and that of sugar increased.

It is best obtained from the liver; the organ is removed as quickly as possible after death, ground or cut into small pieces, which are immediately thrown into boiling water; it should not be subjected to prolonged boiling, but, the water being poured off, the pulp is expressed and the united liquids filtered and evaporated over the water-bath to a small bulk; the cooled solution is precipitated with glacial acetic acid, or, better, with alcohol; the precipitate is collected, redissolved in water; the solution filtered through animal charcoal, and again, after concentration if necessary, precipitated by alcohol.

Pure glycogen is a snow-white, floury powder; amorphous, tasteless, and odorless; soluble in water, insoluble in alcohol and ether; in water it swells up at first, and forms an opalescent solution, which becomes clear on the addition of potash. According to Hoppe-Seyler, its solutions are dextrogyrous to about three times the extent of those of glucose.

Dilute acids, ptyalin, pancreatin, extract of liver-tissue, blood, diastase, and albuminoids convert glycogen into a sugar having all the properties of glucose. Cold nitric acid converts it into xyloidin; on boiling, into oxalic acid. Its solutions dissolve cupric hydrate, which is, however, not reduced on boiling. Iodine colors glycogen wine-red.

Concerning the method of formation of glycogen in the economy, but little is known with certainty; there is little room for doubting, however, that while the bulk of the glycogen found in the liver results from modification of the carbohydrates, it may be and is produced from the albuminoids as well. The ultimate fate of glycogen is undoubtedly its transformation into sugar under the influence of the many substances existing in the body capable of provoking that change.

Dextrin, *British gum*, a substance resembling gum arabic in appearance and in many properties, is obtained by one of three methods: 1st, by subjecting starch to a dry heat of 175°, known as the baking process; 2d, by heating starch with dilute sulphuric acid to 90° until a drop of the liquid gives only a wine-red color, neutralizing with chalk, filtering, concentrating, precipitating with alcohol; the product so obtained almost always contains glucose; 3d, by the action of diastase (infusion of malt) upon hydrated starch; as soon as the starch is dissolved the liquid must be rapidly heated to boiling to prevent saccharification. The product is also usually contaminated with glucose.

Dextrin is a colorless, or yellowish, amorphous powder, soluble in water in all proportions, forming syrupy liquids; when obtained by evaporation of its solution, it forms masses resembling gum arabic in appearance. Dextrogyrous, $[a]_D = +138.88°$.

Nitric acid oxidizes dextrin, not to mucic acid, as it does the gums, but to oxalic acid; a mixture of nitric and sulphuric acids converts it into a dinitro-compound. Dextrin reduces the cupro-potassic solutions at 85°. By iodine it is colored light wine-red.

Dextrin has been found to exist in the blood, lungs and other organs of carnivora and herbivora, and in the contents of the intestine.

Inulin—*Helenin*—*Dahlinin*—*Menyanthin*—a substance resembling starch, obtained from the roots of certain vegetables; it differs from starch in being converted by prolonged contact with boiling water into a lævogyrous, uncrystallizable sugar; in being itself lævogyrous, $[a]_D = -34.4°$ (?), in not being colored blue by iodine, and in reducing, when heated, in the presence of ammonia, the salts of copper and silver.

Tunicin, a cellulose-like substance which constitutes the organic portion of the mantle of certain molluscs. It withstands the action of reagents better than cellulose, but may be converted into a sugar by sulphuric acid.

Cellulose—*Cellulin*—*Lignin*—forms the basis of all vegetable tissues; it exists, almost pure, in the pith of elder and of other plants, in the purer, unsized papers, in cotton, and in the silky appendages of certain seeds. Cotton, freed from extraneous matter by boiling with potash, and afterward with dilute hydrochloric acid, yields pure cellulose.

It is a white material, having the shape of the vegetable structure from which it was obtained; insoluble in the usual neutral solvents, but soluble in the deep blue liquid obtained by dissolving copper in ammonia in contact with air.

By the action of reagents upon cellulose, as paper and cotton, several valuable products are obtained.

Vegetable parchment, or *parchment paper*, a tough material, possessing all the valuable properties of parchment, is made by immersing unsized paper for an instant in moderately strong sulphuric acid, washing thoroughly, and drying.

Nitro-cellulose. By the action of nitric acid upon cellulose, cotton, three different products of substitution may be obtained: *mononitro-cellulose*, soluble in acetic acid, insoluble in a mixture of ether and alcohol; *dinitro-cellulose*, insoluble in acetic acid, soluble in a mixture of ether and alcohol; *trinitro-cellulose*, soluble in both the above solvents. Products known as *gun-cotton* or *pyroxylin*, composed of varying proportions of these three derivatives, are obtained for use in the arts. When gun-cotton is required as an explosive agent, the process is so managed that the product shall contain the greatest possible proportion of trinitro-cellulose, the most readily inflammable of the three. When required for the preparation of collodion for use in medicine or in photography, dinitro-cellulose is the most valuable. To obtain this, a mixture is made of equal weights of nitric and sulphuric acids (of each about five times the weight of the cotton to be treated); in this the cotton is immersed and well stirred for about three minutes, after which it is well stirred in a large vessel of water, washed with fresh portions of water until the washings are no longer precipitated by barium chloride, and dried. *Collodion* is a solution of dinitro-cellulose in a mixture of three volumes of ether and one volume of alcohol.

Gums are substances of unknown constitution, existing in plants; amorphous; soluble in water, insoluble in alcohol; converted into glucose by boiling with dilute sulphuric acid.

Lichenin is obtained from various lichens by extraction with boiling water, forming a jelly on cooling; it is oxidized to oxalic acid by nitric acid; is colored yellow by iodine; and is precipitated from its solutions by alcohol.

Arabin is the soluble portion of gum arabic and gum senegal—*Acacia* (U. S. P.)—in which it exists in combination with potassium and sodium. To separate arabin, gum arabic is dissolved in water acidulated with hydrochloric acid, and precipitated by alcohol. It is a white, amorphous, tasteless substance, which is not colored by iodine; is oxidized by nitric acid to mucic and saccharic acids; is converted by sulphuric acid into a non-fermentable sugar, *arabinose;* and has the composition, $C_{12}H_{20}O_{10}+1$ Aq.

Bassorin constitutes the greater part of gum tragacanth; it is insoluble in water, but swells up to a jelly in that fluid.

Cerasin is an insoluble gum exuded by cherry- and plum-trees; water acts upon it as upon bassorin.

FIFTH SERIES OF HYDROCARBONS.

Series C_nH_{2n-6}.

The hydrocarbons of this series are the starting-points from which the major part of that numerous and important class of substances usually classed as *aromatic* are obtainable or derivable. Those of the series at present known are:

Benzene... C_6H_6 .. boils at 80.4°		Cumene ... C_9H_{12} ... boils at 151.4°	
Toluene ... C_7H_8 .. boils at 110.3°		Cymene ... $C_{10}H_{14}$ .. boils at 175.0°	
Xylene .... C_8H_{10} .. boils at 142.0°		Laurene ... $C_{11}H_{16}$ .. boils at 188.0°	

Benzene.

Benzol—phenyl hydride—C_6H_6 (not to be confounded with the commercial *benzine*, a mixture of hydrocarbons of the series C_nH_{2n+2}, obtained from petroleum).—This important substance, which may be considered as the basis of all the aromatic compounds, was discovered by Faraday in 1825, among the products of the distillation of the fatty oils.

It does not exist in nature, but is produced in a great number of reactions. It is obtained by one of two methods, according as it is required chemically pure or mixed with other substances.

To obtain it pure, recourse must be had to the decomposition of one of its derivatives, benzoic acid; this substance is intimately mixed with three parts of slacked lime, and the mixture heated to dull redness in an earthenware retort connected with a well-cooled receiver; the upper layer of distilled liquid is separated, shaken with potassium hydrate solution, again separated, dried by contact with fused calcium chloride, and redistilled over the water-bath.

For use in the arts, and for most chemical purposes, benzene is obtained from coal- or gas-tar, an exceedingly complex mixture, containing some forty or fifty substances, among which are:

Hydrocarbons.		Acids.	Bases.	
Benzene.	Acenaphthalene.	Carbolic.	Pyridine.	Iridoline.
Toluene.	Fluorene.	Cresylic.	Aniline.	Cryptidine.
Xylene.	Anthracene.	Phlorylic.	Picoline.	Acridine.
Cumene.	Retene.	Rosolic.	Lutidine.	Coridine.
Cymene.	Chrysene.	Oxyphenic.	Collidine.	Rubidine.
Naphthalene.	Pyrene.		Leucoline.	Viridine.

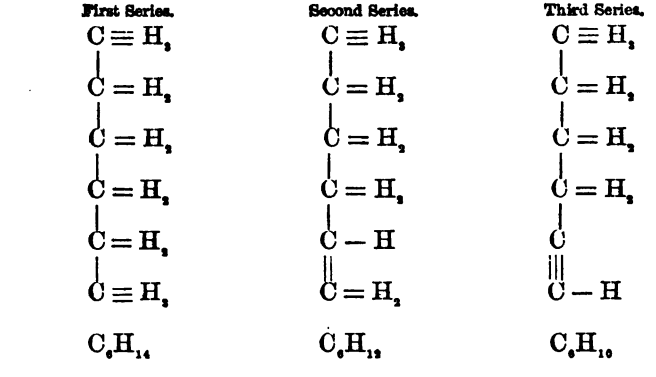
By a primary distillation of coal-tar the most volatile constituents, including benzene, are separated as light oil; this is washed, first with sulphuric acid, and then with caustic soda, and afterward redistilled; that portion being collected which passes between 80° and 85°. This is the commercial benzene, a product still contaminated with the higher homologues of the same series, from which it is almost impossible to separate it, but whose presence is rather advantageous than otherwise to the principal use to which benzol is put—the manufacture of aniline dyes.

Benzene is a colorless, mobile liquid, having, when pure, an agreeable odor; sp. gr. 0.86 at 15°; crystallizing at +4.5°; boiling at 80.5°; very sparingly soluble in water, soluble in alcohol, ether, and acetone. It dissolves iodine, sulphur, phosphorus, resins, caoutchouc, gutta-percha, and almost all the alkaloids. It is inflammable, and burns with a luminous, smoky flame.

Benzene unites with chlorine or bromine to form products of addition, or of substitution; the corresponding iodine compounds can only be obtained by indirect methods. Sulphuric acid combines with benzene to form a neutral substance, *sulpho-benzide*, when the anhydrous acid is used, and *phenyl-sulphurous acid* with the ordinary sulphuric acid.

The action of nitric acid upon benzene is of great commercial interest; if fuming nitric acid of sp. gr. 1.52 be slowly added to benzene, a reddish liquid is formed; from which, on the addition of water, a reddish yellow oil separates, and is purified by washing with water and with sodium carbonate solution, drying and rectifying; this oily material is *mononitro-benzene* (see pp. 319, 333). If benzol be boiled with fuming nitric acid, or if it be dropped into a mixture of nitric and sulphuric acids, so long as the fluids mix, a crystalline product, *dinitro-benzene*, is formed.

The constitution of benzene, the nucleus of the aromatic compounds, differs much in character from that of the hydrocarbons of the series hitherto considered, and is of importance in connection with the formation of its numerous derivatives. Writing the molecular formulæ of the sixth of each of the first three series (the constitution of those of the terebenthene series is still doubtful) we have:

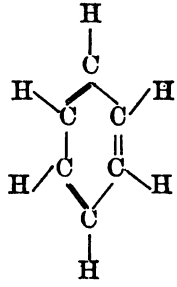


and those of the second term (the first being necessarily absent in the second and third series):

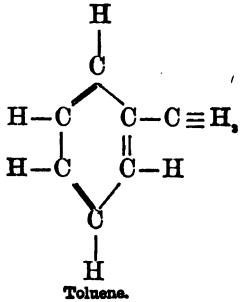
$C \equiv H_2$	$C = H_2$	$C - H$
$\vert$	$\Vert$	$\vert\vert\vert$
$C \equiv H_2$	$C = H_2$	$C - H$
C_2H_6	C_2H_4	C_2H_2
C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}

It will be observed that in each of these the chain of carbon atoms is an open one, and that the series differ in this, that in the first, each of the atoms of carbon exchanges with its neighbor a single valence; in the second, two neighboring carbon-atoms exchange two valences between them; and that in the third there is an exchange of three valences between two neighboring carbon-atoms. And, further, that in terms above the second in the first two series, and the third in the third series, superior homologues may be considered as formed by interpolation of CH_2 in the chain of the one next below.

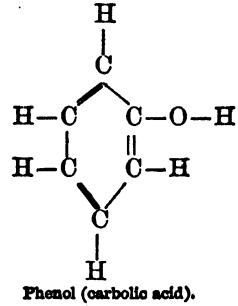
In the case of benzene, Kekulé has advanced the theory, according to which alone the formation of the benzene derivatives can be explained, and against whose adoption no reason based upon experiment has been advanced; that the carbon atoms of the benzene molecule are arranged, not in an open, but a closed chain, that they exchange with each other alternately one and two valences, and that consequently the molecular formula of benzol is:



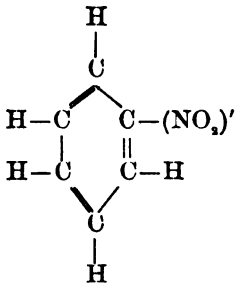
Further, that the superior homologues of benzene are derived from it by the substitution of CH_3 for H, and that all the derivatives of benzol are formed by such substitution of a group or groups for an atom or atoms of hydrogen, in such a way that they all contain one or more groups of six atoms of carbon arranged as above:



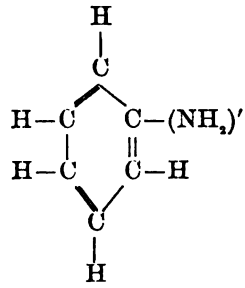
Toluene.



Phenol (carbolic acid).



Nitro-benzene.



Amido-benzene (aniline).

Toluene.

Toluol—Methyl-benzene—$C_6H_5CH_3$—exists in the products of distillation of wood, coal, etc., and as one of the constituents of commercial benzene; in Rangoon tar, a native mineral oil. It has been formed synthetically by acting upon a mixture of monobromo-benzene and methyl iodide with sodium. It is obtained, with considerable difficulty, by fractional distillation from coal-tar.

It is a colorless liquid, having a peculiar odor, differing somewhat from that of benzene; boils at 110.3°; does not solidify at −20°; sp. gr. 0.872 at 15°; almost insoluble in water, soluble in alcohol, ether, carbon disulphide. It burns with a bright, but very smoky flame.

It yields a number of derivatives similar to those of benzene, among which may be mentioned *nitro-toluene* and *toluidine*, the homologues of nitro-benzene and aniline, which accompany those substances in the commercial products; *cresylol*, the superior homologue of carbolic acid, and *benzylic alcohol.*

Xylene—Xylol—Dimethyl-benzene—$C_6H_4(CH_3)_2$—accompanies its inferior homologues in coal-tar. When pure it is a liquid of an aromatic odor; sp. gr. 0.865 at 20°; boils at 142°; insoluble in water, soluble in ether, benzene, etc., sparingly soluble in alcohol.

There are three isomeric substances having this composition, and differing in the position in which the substituted CH_3 groups are placed. Each of these corresponds to a series of derivatives parallel to those of benzene.

Cumene—*Cumol—Propyl-benzene*—$C_6H_5(C_3H_7)$—is obtained by distilling a mixture of cuminic acid and lime, as benzene is prepared from benzoic acid. It is a limpid liquid, having a strong aromatic odor; boils at 151.4°; insoluble in water, very soluble in alcohol and ether.

There are several isomeres of this substance, among which are *pseudocumene*, or *trimethyl-benzene*, $C_6H_3(CH_3)_3$, and *mesitylene*, or *methyl-ethyl-benzene*, $C_6H_4(CH_3)(C_2H_5)$; each corresponding to a series of derivatives.

Cymene—*Cymol*—there are many isomeres, of which one exists ready formed in essence of cumin, and in hemlock. It is a colorless, oily liquid; has an odor of lemon; sp. gr. 0.857 at 16°; boils at 175°; insoluble in water, but readily soluble in alcohol, ether, and essential oils.

Laurene—is an imperfectly studied body, obtained by the decomposition of camphor by zinc chloride. It is a colorless liquid, boiling at 188°; sp. gr. 0.887 at 10°.

Nitro-derivatives.

The products of this class are quite numerous, among them the only one calling for consideration here is:

Nitro-benzene—*nitro-benzol—mono-nitro-benzene—essence of Mirbane*—$C_6H_5(NO_2)$—this important substance, whose production lies at the root of the aniline industry, was discovered by Mitscherlich, and is formed by the action of nitric acid upon benzene.

Benzol is slowly added to fuming nitric acid, or to a mixture of nitric and sulphuric acids, care being taken to agitate the mixture and to prevent elevation of temperature; the nitro-benzene formed is decanted, repeatedly washed with solution of sodium carbonate and with water. The result of this process is sufficiently pure for industrial uses; if required in a state of greater purity, it may be distilled—a process, however, attended with considerable loss.

Nitro-benzene is a yellowish liquid; has a sweet taste and a pronounced odor of bitter almonds; sp. gr. 1.209 at 15°; boils at 213°; almost insoluble in water, very soluble in alcohol and ether.

Chlorine and bromine do not attack it at ordinary temperatures. Concentrated sulphuric acid dissolves it, and, at the boiling temperature, decomposes it; boiled with fuming nitric acid, it is converted into binitro-benzene; with ordinary nitric or sulphuric acid, it may be distilled unchanged. It is attacked by potash with difficulty.

The most important reaction of nitro-benzene is that with reducing agents; a great number of which convert it into aniline (*q. v.*).

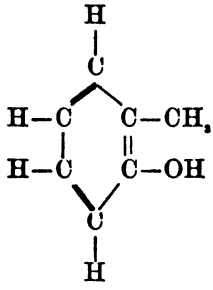
Under the names *essence of mirbane* and *artificial essence of bitter almonds*, this substance has been used in perfumery to a considerable extent—a use which cannot be too strongly condemned, as nitro-benzol is, as well in the form of vapor as in that of liquid, an active poison. When taken internally, even in a dose of a few drops, it has caused death in several instances, although recovery has followed the taking of a considerably larger dose. Inhalation of its vapor, even when largely diluted with air, produces headache, drowsiness, difficulty of respiration, cardiac irregularity, more or less loss of muscular power, convulsions, coma. Obviously, the frequent inhalation, even in small quantities, of a substance such as this, is to be avoided.

Nitro-benzol can be distinguished from benzoic aldehyde by sulphuric acid, which does not color the former; and by the action of acetic acid and iron filings, which convert nitro-benzene into aniline, whose presence is indicated by the reactions on p. 333.

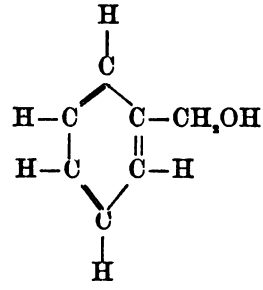
Phenols.

The hydrocarbons of this series, unlike those previously considered, form by substitution two distinct series of hydrates, which differ from each other materially in their properties. The terms of one of these series possess all the functions of the alcohols, and are therefor known as the aromatic alcohols (see p. 323). The terms of the other series differ in function from any substance thus far considered, and are known as *phenols*, the difference between them and the aromatic alcohols being

probably due to the fact that in the phenols the OH is directly attached to a carbon atom, while in the alcohols it is substituted for an atom of hydrogen of a substituted hydrocarbon group, thus:



Benzylic phenol.



Benzylic alcohol.

The phenols differ from the alcohols in many particulars: in not furnishing by oxidation corresponding aldehyds and acids; in not dividing into water and hydrocarbon under the influence of dehydrating agents; in not reacting with acids to form ethers; in combining to form directly products of substitution with chlorine, bromine and nitrosyl; and in forming with metallic elements compounds more stable than similar compounds of the true alcohols. In short, the phenols appear to have, besides an alcoholic function, more or less of the function of acids.

Phenol.

Phenyl hydrate—Phenic acid—Carbolic acid—Acidum carbolicum (U. S., Br.) C_6H_5OH—exists in considerable quantity in coal- and wood-tar, and in small quantity in castoreum, and possibly in urine.

It is formed in a number of reactions: 1st, by fusing sodium phenylsulphite with an excess of alkali; 2d, by heating phenyl iodide with potassium hydrate to 320°; 3d, by heating together salicylic acid and quicklime; 4th, by total synthesis from acetylene; 5th, by dry distillation of benzoin.

The source from which it is exclusively obtained is coal-tar, or rather that portion of the product of distillation of coal-tar which passes over between 150° and 200°. This is treated with a saturated solution of potash containing undissolved alkali; a solid phenate is formed, which is dissolved in hot water; the liquid is allowed to separate into two layers, the lower of which is drawn off and neutralized with hydrochloric acid; the phenol rises to the surface, is separated, washed with water, dried over calcium chloride, redistilled, crystallized at −10°, and the crystals drained.

Pure phenol crystallizes in long, colorless, prismatic needles, fusible at 35°, boiling at 187°. It has a peculiar, well-known odor, and an acrid, burning taste; very sparingly soluble in water, readily soluble in alcohol and in ether; sp. gr. 1.065 at 18°; neutral in reaction. On contact with the skin or with mucous surfaces, it produces a white stain; it coagulates albuminoids, and is a powerful antiseptic.

Phenol is capable of distillation without decomposition, and at a red heat is only partially decomposed, with formation of a small quantity of naphthalin. On contact with damp air it absorbs moisture to form a hydrate, which crystallizes in six-sided prisms, fusible at 16°, which loses its water at 187°. Vapor of phenol is reduced to benzene when heated with zinc-filings.

It combines with sulphuric acid to form sulpho-conjugate acids (phenylsulphuric acids). With concentrated hydriodic acid at 280° it yields benzene. Nitric acid converts it into nitro-derivatives, differing with the concentration of the acid used; with an acid of 36° B. it forms *trinitrophenic* or *picric acid* (*q. v.*). When heated with sulphuric and oxalic acids, it forms a colored substance known as *corallin* or *rosolic acid;* this is a mixture from which several beautiful pigments, *aurin*, *peonin*, *azulin*, and *phenicin*, are obtained.

Phenol may be recognized by the following reactions: 1st, its peculiar odor; 2d, the formation of the yellow picric acid with nitric acid of 36° B.; 3d, the production of a blue or green color when treated with a small quantity of ammonium hydrate and a trace of solution of a hypochlorite; 4th, a lilac color produced on the addition of a small quantity of ferric sulphate; 5th, a yellowish white precipitate with bromine water; 6th, precipitation of albuminoids. Of these reactions, 3d, 4th, and 5th are very delicate.

Toxicology.—The use of carbolic acid in medicine, both for external use as one of the most valuable of antiseptics, and for internal administration, has of late years become widely extended. The energy of its caustic action upon living tissues, and of its power of coagulation of the albuminoids, render it very actively injurious when taken internally, and although its odor prevents, in a great measure, its ingestion by mistake, or its administration with murderous intent; yet such cases have occurred, and instances in which it is taken suicidally are becoming exceedingly common. Woodman and Tidy cite twenty-one cases of poisoning by phenol occurring during the years of 1868 to 1873, among which there was but one recovery, the doses taken being usually one to two ounces, a quantity certainly much greater than the minimum lethal dose; in one instance death followed the application of carbolic acid to a wound.

When this poison has been taken, the mouth is whitened by its caustic action; there is a marked odor of carbolic acid in the breath. The acid is eliminated by the urine, partly unchanged, and partly in the form of colored derivatives, which communicate to the urine a greenish, brownish, or even black colour; biliary acids are also usually present.

The treatment consists in the administration of albumen (white of egg) and of emetics.

To detect phenol in the urine, that liquor must not be distilled with sulphuric acid, as sometimes recommended, as it contains normally substances which by such treatment yield carbolic acid. The best method is that of Landolt, which consists in adding an excess of bromine water to about 500 c.c. of the urine; on standing some hours, a yellowish precipitate collects at the bottom of the vessel; this is removed, washed, and treated with sodium amalgam, when the characteristic odor of phenol is developed. From other parts of the body, phenol may be recovered by acidulating with tartaric acid; distilling; extracting the distillate by shaking with ether; evaporating the ethereal solution; extracting the residue with a small quantity of water, and applying to this solution the tests described above.

Trinitrophenol—*Picric acid*—*Trinitrophenic acid*—$C_6H_2(NO_2)_3OH$.—This substance, the method of whose formation has been given above, is derived from phenol by the substitution of three groups (NO_2) for three atoms of hydrogen; it is the only one of the numerous substitution products of phenol which is of sufficient medical interest for consideration here.

It crystallizes in brilliant, yellow, rectangular plates, or in six-sided prisms; it is odorless, and has an intensely bitter taste, whence its more common name (from πικρὸς=bitter); it is acid in reaction; sparingly soluble in water, very soluble in alcohol, ether, and benzene; it fuses at 122.5°, and may, if heated with caution, be sublimed unchanged; but, if heated suddenly or in quantity, it explodes with violence.

Trinitrophenol behaves as a monobasic acid, forming salts, which are for the most part soluble, yellow, crystalline, and decompose with explosion when heated.

The presence of picric acid is detected by: 1st, its intensely bitter taste; 2d, its alcoholic solution when shaken with a potassium salt gives a yellow crystalline precipitate; 3d, an ammoniacal solution of cupric sulphate gives a green, crystalline precipitate; 4th, glucose heated with a dilute alkaline solution of picric acid, communicates to it a blood-red color; 5th, warmed with an alkaline solution of potassium cyanide, an intense red color is produced (the same effect is produced by ammonium sulphydrate); 6th, unbleached wool, immersed in boiling solution of picric acid, is dyed yellow. Nos. 1, 3, 5 and 6 are quite delicate.

Picric acid stains animal tissues yellow, and is used for that purpose by histologists. It is largely used for dyeing; is fraudulently added to beers to render them bitter; and is of value in toxicological analysis, as it precipitates the alkaloids from their solutions.

When taken internally in overdose, it acts as a poison; it may be separated from animal fluids or from beer by evaporating to a syrup, extracting with 95 per cent. alcohol, acidulated with sulphuric acid; filtering; evaporating; and applying the above-mentioned tests to a solution of the residue.

Cresylol.

Cresol—*Cresylic acid*—*Benzylic phenol*—*Cresylic phenol*—$C_6H_4(CH_3)OH$—accompanies phenol in coal- and wood-tars, from which it may be obtained by fractional distillation; it is more readily obtained pure from toluene.

When pure it is a crystalline solid, fusible at 34.5°; as usually met with, however, it is a liquid, which does not solidify at −18°, and boils at 203°; it has an odor of creasote. Its properties, decompositions and products resemble those of phenol.

Creasote is a complex mixture, containing phenol, cresylol, *creasol*, $C_8H_{10}O_2$, and other substances obtained from wood-tar, and formerly extensively used as an antiseptic. It is an oily liquid, colorless when freshly prepared, but becoming brownish on exposure to light; it has a burning taste and a strong, peculiar odor; its specific gravity is variously stated from 1.037 to 1.087 at 20°; it boils at 203°, and does not solidify at −27°.

Crude phenol is often substituted for creasote; the two substances may be distinguished by the following characters:

PHENOL.	CREASOTE.
Soluble in commercial glycerin.	Insoluble in commercial glycerin.
Precipitates nitro-cellulose from collodion.	Does not precipitate collodion.
Gives a brown color with ferric chloride and alcohol.	Gives a green color with ferric chloride and alcohol.
Gives a violet color with ferric chloride and ammonium hydrate.	Gives a green color, passing to brown, with ferric chloride and ammonium hydrate.

Xenols—*Xylenols*—$C_6H_3(CH_3)_2OH$.—Theoretically there are six possible xenols, derivable from corresponding xylenes; of these, four have been thus far obtained by the general methods of obtaining the phenols. None is of practical interest.

Thymol—*Cymylic phenol*—$C_6H(CH_3)_4OH$, exists, accompanying cymene and thymene, $C_{10}H_{16}$, in essence of thyme, from which it was first and is still obtained; the essence contains about one-half its weight of thymol, which is separated by agitation with a concentrated solution of caustic soda; separation of the alkaline liquid, which is diluted and neutralized with hydrochlorie acid; thymol separates and is purified by rectification at 230°.

It crystallizes in large, transparent, rhombohedral tables; has a peppery taste and an agreeable, aromatic odor; it fuses at 44° and boils at 230°; is sparingly soluble in water, very soluble in alcohol and ether; with the alkalies it forms definite compounds, which are very soluble in water. Its reactions are very similar to those of phenol.

Thymol is an excellent disinfecting and antiseptic agent, and one of the best of embalming materials; possessing the advantage over phenol of having itself a pleasant odor, while that of phenol is disagreeable to most persons.

Aromatic Alcohols.

The alcohols corresponding to this series of hydrocarbons have the same composition as the corresponding phenols, from which they differ in constitution and in having the function of true alcohols (see p. 150). The first of the series is:

Benzylic alcohol—*Benzoic alcohol*—*Benzyl hydrate*—$C_6H_5(CH_2OH)$—does not exist in nature, and is of interest chiefly as corresponding to two important compounds, benzoic acid and benzoic aldehyde (oil of bitter almonds). It is obtained by the action of potassium hydrate upon oil of bitter almonds, or by slowly adding sodium amalgam to a boiling solution of benzoic acid.

It is a colorless liquid; sp. gr. 1.05 at 14.4°; boils at 206.5°; has an aromatic odor; is insoluble in water, soluble in all proportions in alcohol, ether, and carbon disulphide

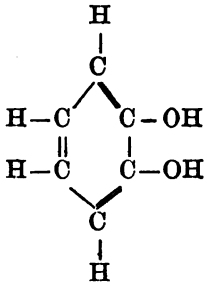
By oxidation it yields, first, benzoic aldehyde, $C_6H_5(COH)$; and afterward, benzoic acid, $C_6H_5(COOH)$. By the same means it may be made to yield products similar to those obtained from the alcohols of the saturated hydrocarbons.

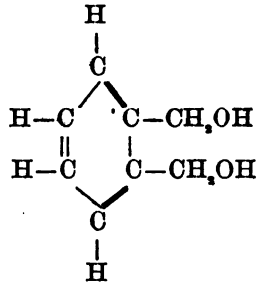
The remaining alcohols of this series are:

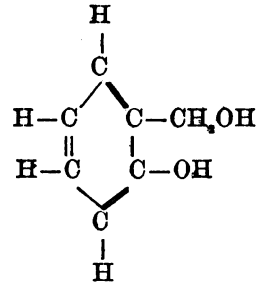
Xylylic alcohol.....$C_6H_5(CH_2-CH_2OH)$.
Cumylic alcohol.....$C_6H_5(CH_2-CH_2-CH_2OH)$.
Cymylic alcohol.....$C_6H_5(CH_2-CH_2-CH_2-CH_2OH)$.

Diatomic Aromatic Hydrates.

There are three classes of these substances, viz.: Diatomic phenols, diatomic alcohols, and *alphenols*, which last are substances having a mixed function of alcohol and phenol, thus:


Hydroquinone (diatomic phenol).


Toluyl glycol (diatomic alcohol).


Saligenin (alphenol).

Phenols—*Oxyphenols.*—There exist three different compounds of the composition $C_6H_6O_2$.

Pyrocatechin, a crystalline solid, fusible at 112°, boiling at 240°, has a powerful odor; soluble in water and alcohol; obtained by the dry distillation of kino and catechu.

Resorcin, colorless, prismatic crystals, fusible at 110°, boiling at 270°; obtained by the action of potash on galbanum, assafetida, etc.

Hydroquinone, transparent, colorless prisms, fusible at 177.5°; soluble in water, alcohol, and ether; obtained by the action of reducing agents on quinone.

Quinone, $C_6H_4\begin{matrix}/O\\ |\\ \backslash O\end{matrix}$—is formed by the action of oxidizing agents on quinic acid (*q. v.*); it crystallizes in long, transparent needles, fusible at 115.7°; very soluble in water, alcohol, and ether; very volatile, emitting irritating vapors at all temperatures; its solution stains the skin brown.

Orcin, $C_7H_8O_2$, the superior homologue of hydraquinone, is obtained from lichens of the genus *Rocella*. It forms white, crystalline needles, fusing at 86°, boiling at 280°—287°; sweet in taste; soluble in water, alcohol, and ether. Anhydrous orcine absorbs dry ammonia, forming large, colorless crystals, which, although permanent in a dry vacuum, rapidly absorb moisture from the air and are converted into *orcein*, $C_7H_7NO_3$, the coloring matter of orchil and litmus.

Saligenin, $C_6H_4\begin{matrix}/CH_2OH\\ \backslash OH\end{matrix}$—is an *alphenol, i.e.*, a substance partly alcohol (by the group CH_2OH) and partly phenol. It is obtained from salicine (*q. v.*) in large, tabular crystals; quite soluble in alcohol, water and ether. Oxidizing agents convert it into salicylic aldehyde, which by further oxidation yields salicylic acid.

Toluyl glycol, $C_6H_4\begin{matrix}/CH_2OH\\ \backslash CH_2OH\end{matrix}$—the only one of the diatomic, aromatic alcohols at present known; has been recently obtained by Gri-

maux, by saponifying the corresponding chloride or bromide; it forms opaque, crystalline needles; very soluble in water. By oxidation with potassium dichromate and sulphuric acid, it yields *terephthalic acid.* (See below.)

Triatomic Aromatic Hydrates.

The only compounds of this class at present known with certainty are two isomeric triatomic phenols, which probably owe the differences in properties existing between them to a different placing of the OH groups. They are *phloroglucin* and *pyrogallol.*

Phloroglucin, $C_6H_3(OH)_3$—is obtained by the action of potash upon phloretin, quercitrin, maclurin (see Glucosides), catechin, kino, etc. It crystallizes in rhombic prisms, containing 2 Aq.; is very sweet; very soluble in water, alcohol, and ether.

Pyrogallol—Pyrogallic acid—$C_6H_3(OH)_3$—is formed when gallic acid (*q. v.*) is heated to 200°; it crystallizes in white needles; neutral in reaction; very soluble in water; very bitter; fuses at 115°; boils at 210°; poisonous. Its most valuable property is that of absorbing oxygen from the air, for which purpose it is used in the laboratory in the form of a solution of potassium pyrogallate.

Acids Corresponding to the Aromatic Hydrates.

The acids, possibly derivable from benzene by the substitution of (COOH), or of (COOH) and (OH), for atoms of hydrogen, would form, were they all known, a great number of series; there are, however, comparatively few of them which have been as yet obtained, although the number of acid series known is greater than that of corresponding alcohols. Each series of mono- and diatomic alcohols furnishes a corresponding series of acids; thus:

$C_6H_5-CH_2OH$	$C_6H_4\begin{cases}CH_2OH\\CH_2OH\end{cases}$	$C_6H_4\begin{cases}CH_2OH\\OH\end{cases}$
Benzoic alcohol.	Tolnyl glycol.	Saligenin.
C_6H_5-COOH	$C_6H_4\begin{cases}COOH\\COOH\end{cases}$	$C_6H_4\begin{cases}COOH\\OH\end{cases}$
Benzoic acid.	Terephthalic acid.	Salicylic acid.

There are still a number of other series of acids possibly derivable directly from benzene, without speaking of substituted acids of more complex nature; of these, however, the majority are wanting.

By the progressive substitution of groups (COOH) for atoms of hydrogen in benzene, we may obtain six series of acids, five of which have been isolated:

$C_6H_5(COOH) - C_nH_{2n-8}O_2$ ..... Benzoic series.
$C_6H_4(COOH)_2 - C_nH_{2n-10}O_4$ ..... Phthalic series.
$C_6H_3(COOH)_3 - C_nH_{2n-12}O_6$ ..... Trimellitic series.
$C_6H_2(COOH)_4 - C_nH_{2n-14}O_8$ ..... Prehnitic series.
$C_6H(COOH)_5 - C_nH_{2n-16}O_{10}$ ..... Wanting.
$C_6(COOH)_6 - C_nH_{2n-18}O_{12}$ ..... Mellitic series.

The alphenols, containing a single group (OH), are at present represented by a single series:

$$C_6H_4(OH)(COOH)—C_nH_{2n-8}O_3—\text{Salicylic series.}$$

Corresponding to the unknown alphenols, containing a greater number of (OH) groups, there are at present but two series of acids known:

$$C_6H_2(OH)_2(COOH)—C_nH_{2n-8}O_4—\text{Veratric series,}$$

and

$$C_6H_2(OH)_3(COOH)—C_nH_{2n-8}O_5—\text{Gallic series.}$$

In each of these series the basicity is, as usual, equal to the number of groups (COOH).

Benzoic Series, $C_nH_{2n-8}O_2$.

The acids of this series (which are, as the formula above indicates, monobasic) at present known are:

Benzoic acid.....$C_7H_6O_2$	Cumic acid.....$C_{10}H_{12}O_2$
Toluic acid.....$C_8H_8O_2$	*a* Cymic acid.....$C_{11}H_{14}O_2$
Xylic acid.....$C_9H_{10}O_2$	

Benzoic acid, $C_6H_5(COOH)$—one of the earliest known of organic acids, having been obtained by sublimation from benzoin. It exists ready formed in benzoin, tolu balsam, castoreum, and several resins (see p. 297), it does not exist in animal nature, so far as is at present known; in those situations in which it has been found, it has resulted from decomposition of hippuric acid (*q. v.*), or has been introduced from without. When taken in moderate doses, it does not pass out in its own form, but is converted into hippuric acid; in excessive doses a portion is eliminated, unchanged, in the urine.

Benzoic acid is obtained by one of two processes: 1st. For use in medicine, it is extracted from benzoin, which is boiled for some hours with milk of lime; the solution of calcium benzoate so formed is filtered off and decomposed with hydrochloric acid; the precipitated acid is washed and purified, either by recrystallization from boiling water, or by sublimation; in the latter case the crude acid is heated in a porcelain dish, over which is placed a sheet of filter-paper, and over that a cone of bristol-board, which acts as a condenser. The process formerly followed, by direct sublimation of benzoin, is not as advantageous. 2d. For use in the arts, benzoic acid is obtained from the urine of herbivorous animals; this is boiled with hydrochloric acid, and treated with milk of lime, the calcium salt is decomposed, and the liberated acid purified as above. The acid prepared by this process retains tenaciously an odor of urine, which may be removed to a great extent by distilling with a little benzoin.

Benzoic acid is formed in a variety of reactions, among others by synthesis from benzene; this is converted into its monobromo-derivative, which is mixed with sodium and treated with carbon dioxide:

C_6H_5Br	+	Na_2	+	CO_2	=	$C_7H_5O_2Na$	+	$NaBr$
Monobromo-benzene.		Sodium.		Carbon dioxide.		Sodium benzoate.		Sodium bromide.

a general reaction, by which several other acids are obtained from corresponding hydrocarbons.

Pure benzoic acid crystallizes in white, transparent, pearly plates or needles; odorless (the pharmaceutical product usually has a faint odor of benzoin); acid in taste; fuses at 122°; sublimes at 145°; boils at 240°; sparingly soluble in cold water, soluble in twelve parts of boiling water, very soluble in alcohol and ether.

Dilute nitric and chromic acids do not attack benzoic acid. It dissolves in ordinary sulphuric acid, and may be precipitated from the solution, unchanged, by the addition of water; Nordhausen sulphuric acid converts it into *sulphobenzoic acid.* Fuming nitric acid forms with it *nitrobenzoic acid;* and a mixture of fuming nitric and sulphuric acids *binitrobenzoic acid.* Under the influence of sodium amalgam, it yields benzylic alcohol and other products. Distilled with an excess of lime or baryta, it yields carbon dioxide and benzene.

The salts of benzoic acid are all soluble, those of the heavy metals less so than those of the alkaline metals.

The radical of benzoic acid $(C_7H_5O)'$, is known as benzoyl; it enters into a number of compounds similar to those of acetyl $(C_2H_3O)'$; thus we have a hydride C_7H_5OH; a chloride, C_7H_5OCl; an amide, $C_7H_5ONH_2$.

Intimately connected with benzoic acid is **Hippuric acid**—*Benzylglycocol—Benzyl-amido-acetic acid*—$C_9H_9NO_3$—a constant constituent of the urine of the herbivora. In human urine, with normal food, it exists in small quantity; with a purely vegetable diet, its elimination is greatly increased, as it is also after the administration of benzoic acid, and, to a less degree, in diabetes mellitus and in chorea. The amount of hippuric acid eliminated under normal circumstances by man varies from 0.29 gram to 2.84 grams in twenty-four hours.

Hippuric acid is extracted from the urine of the horse, cow, etc.; this is concentrated to a syrup and treated with two to three times its bulk of hydrochloric acid; the highly colored deposit of hippuric acid is converted into sodium hippurate; the solution, decolorized with a little hypochlorite solution, and again precipitated with hydrochloric acid; if required pure, it must be further decolorized by boiling with animal charcoal, and recrystallization.

It crystallizes in colorless, transparent prisms; odorless; faintly bitter; sparingly soluble in cold water, less so in the presence of hydrochloric acid, more so in the presence of hydrodisodic phosphate, very soluble in boiling water and in alcohol, insoluble in ether; fuses at 130°; boils at 240°; at a slightly higher temperature it is decomposed, with formation of benzoic and hydrocyanic acids.

To understand the reactions of hippuric acid, a knowledge of its constitution is necessary. It has been long known that hippuric acid may be decomposed into glycocol (see page 208) and benzoic acid. Later, by the action of nitrous acid upon hippuric acid, an acid having the constitution of glycolic acid, in which the alcoholic hydrogen is replaced by benzoyl (see above) was obtained, and designated as *benzoglycolic acid.* Finally, hippuric acid has been obtained synthetically by the action of benzoyl chloride upon silver glycolamate:

$$\underset{\text{Silver glycolamate.}}{C_2H_2(NH_2)O_2Ag} + \underset{\substack{\text{Benzoyl}\\\text{chloride.}}}{C_7H_5OCl} = \underset{\substack{\text{Hippuric}\\\text{acid.}}}{C_9H_9NO_3} + \underset{\substack{\text{Silver}\\\text{chloride.}}}{AgCl}$$

And again, hippuric acid has been obtained by the action of benzamide

upon chloracetic acid. Now, glycocol is derivable from glycolic acid by the substitution of NH_2 for OH; or from chloracetic acid by the substitution of NH_2 for Cl:

CH_2OH	CH_2Cl	$CH_2(NH_2)$
COOH	COOH	COOH
Glycolic acid.	Chloracetic acid.	Amido-acetic acid (glycocol).

The foregoing decompositions and syntheses show that hippuric acid is glycocol in which the radical benzoyl has been substituted for one H of the group NH_2; it is therefor:

$$CH_2(NH[C_7H_5O])$$
$$COOH$$

Benzyl-glycocol or benzyl-amido-acetic acid.

Hippuric acid dissolves unchanged in concentrated hydrochloric acid; on boiling the solution it is decomposed into benzoic acid and glycocol; the same decomposition is effected by dilute sulphuric, nitric, and oxalic acids, and also by a ferment developed in putrefying urine. Concentrated sulphuric acid forms a brown solution with hippuric acid, which, on the application of heat, gives off sulphur dioxide and benzoic acid. Nascent hydrogen produces a number of derivatives from hippuric acid, among which are benzoic aldehyde and glycocol. Oxidizing agents convert it into benzoic acid, carbon dioxide, and benzamide.

The determination of hippuric acid in urine is a tedious process. About a litre of the urine is precipitated with baryta water; filtered; the excess of barium removed from the filtrate by cautious addition of sulphuric acid, avoiding an excess; the filtrate is *neutralized* with hydrochloric acid and evaporated to a syrup; this is extracted with alcohol; the alcoholic solution decanted and evaporated over the water-bath; the residue repeatedly washed with ether; dissolved in warm water and heated with a little milk of lime; filtered, the filtrate decomposed with hydrochloric acid; the crystals which separate are washed with a small quantity of water, dried, and weighed. It is usually necessary to redissolve the acid in water, decolorize with animal charcoal, and reprecipitate before weighing.

The characters of hippuric acid are: 1st, when heated in a dry tube, it fuses and decomposes, giving a sublimate of benzoic acid and an odor of hydrocyanic acid (*q. v.*); 2d, it gives a brown precipitate with ferric salts (so do benzoic and succinic acids); 3d, when heated with lime, it gives off benzene and ammonia. Benzoic acid, by similar treatment, gives off benzene, but no ammonia.

The remaining acids of the benzoic series are not of medical interest. The number of their isomeres is great.

Phthalic Series, $C_nH_{2n-10}O_4$.

Phthalic acid, $C_8H_6O_4$, and its isomeres, *terephthalic* and *isophthalic* acids, are the only ones of this series at present known. Phthalic acid is obtained by the action of nitric acid upon naphthalene or alizarin

(*q. v.*). It crystallizes in white prisms; sparingly soluble in water, very soluble in alcohol and ether; it fuses at 180°, and at a higher temperature is decomposed into phthalic anhydride, $C_6H_4(CO)_2O$, and water; by cautious heating it is decomposed into carbon dioxide and benzoic acid, a reaction which is utilized to obtain the last-named acid.

Salicylic Series, $C_nH_{2n-8}O_3$.

The acids of this series (which are, as indicated by the formula on p. 325, partly phenols, partly acids) are the following:

Salicylic acid ..... $C_7H_6O_3$	Oxycuminic acid ..... $C_{10}H_{12}O_3$
Anisic acid ..... $C_8H_8O_3$	Thymotic acid ..... $C_{11}H_{14}O_3$
Phloretic acid ..... $C_9H_{10}O_3$	

Salicylic Acid—*Oxybenzoic acid*—C_6H_4 (OH) COOH—was first obtained from essence of *spiræa*, which consists largely of salicylic aldehyde, and subsequently from oil of wintergreen (*gaultheria*), which contains methyl salicylate; and also from *salicine*, a glucoside yielding salicylic aldehyde.

At present salicylic acid is obtained almost exclusively by Kolbe's method, from phenol. This is fused, and while a current of dry carbon dioxide is passed through it, small portions of sodium are added; the sodium salicylate thus formed is dissolved in water and decomposed with hydrochloric acid, when the liberated salicylic acid is precipitated.

It crystallizes in fine white needles (the pharmaceutical product is usually pink); very sparingly soluble in cold water, quite soluble in hot water, alcohol, and ether; it fuses at 158°, and may be distilled with but slight decomposition, if it be pure.

Chlorine and bromine form with it products of substitution. Fuming nitric acid forms with it a nitro-derivative and, if the action be prolonged, converts it into picric acid. With ferric chloride, its aqueous solution assumes a fine violet color.

Salicylic acid and its salts (it is monobasic, although diatomic) are extensively used in medicine, both externally as antiseptics and internally in the treatment of rheumatism, etc. It is not without caustic properties, and hence, when taken internally, it should be largely diluted.

Trimellitic Series, $C_nH_{2n-12}O_6$.

There are no less than three isomeric *acids* having the composition of the first term of this series, all of which are tribasic:

Trimellitic acid, C_6H_3 (COOH)$_3$—obtained by heating *hydropyromellitic acid* with sulphuric acid, isophthalic acid being formed at the same time; also formed when rosin is oxidized with nitric acid. Fuses at 216°.

Trimesitic acid—formed by the oxidation of *mesitylenic acid;* fuses at a temperature above 300°.

Hemimellitic acid—formed, along with phthalic acid, by heating *hydromellophanic acid* with sulphuric acid; fuses at 185°.

Prehnitic Series, $C_nH_{2n-14}O_8$.

Of this series there are also three isomerides of the first term; all tetrabasic:

Prehnitic acid, $C_6H_2(COOH)_4$—fuses at 237°.

Pyromellitic acid—formed by the distillation of mellitic acid.

Mellophanic acid—obtained, along with prehnitic acid, by decomposing *hydromellitic acid*, $C_{12}H_{12}O_{12}$.

Mellitic Series, $C_nH_{2n-18}O_{12}$,

is represented by a single term, in which the hydrogen of benzene has been entirely replaced:

Mellitic acid, $C_6(COOH)_6$—occurs in nature as its aluminium salt in the mineral called *mellite* or *honey stone*. It has also been obtained synthetically by oxidizing charcoal with potassium permanganate in alkaline solution.

It crystallizes in colorless needles, readily soluble in water; sour in taste. It withstands the action of reagents well, but by distillation with quicklime is decomposed into benzene and carbon dioxide.

Gallic Series, $C_nH_{2n-8}O_5$.

Gallic acid, $C_6H_2(OH)_3COOH$—the first term and only representative of the series, exists in nature in certain leaves, seeds, and fruits. It is best obtained from gall-nuts which contain its glucoside, gallotannic acid (*q. v.*). These galls are moistened and kept at a temperature of 20°—25°, being moistened from time to time, for a month; the colored, mouldy mass is strongly expressed and the residue extracted with boiling water, which, on cooling, deposits crystals of gallic acid. It can be obtained from salicylic acid.

It crystallizes in long, silky needles; odorless; acidulous in taste; sparingly soluble in cold water, very soluble in hot water and in alcohol; its solutions are acid. When heated to 210°—215° it yields carbon dioxide and pyrogallol (*q. v.*). Its solution does not precipitate gelatin, nor the salts of the alkaloids, as does tannin. It forms four series of salts.

Aldehydes.

Benzoic aldehyde—*Benzoyl hydride*—$C_6H_5(COH)$—is the main constituent of oil of bitter almonds, although it does not exist in the almonds (see p. 342); it is formed, along with hydrocyanic acid and glucose, by the action of water upon amygdalin. It is also formed by a number of general methods of producing aldehydes: by the dehydration of benzylic alcohol; by the dry distillation of a mixture in molecular proportions of calcium benzoate and formiate; by the action of nascent hydrogen upon benzoyl cyanide, etc.

It is obtained from bitter almonds; these are crushed and freed from

fixed oil by expression; the cake is mixed with a large quantity of water, in which it remains twenty-four hours, after which the mixture is distilled by steam heat as long as the distillate has the odor of bitter almonds; the oil separates from the watery liquid, which still contains a considerable quantity in solution, recoverable by a second distillation. This crude oil contains, besides benzoic aldehyde, hydrocyanic and benzoic acids and cyanobenzoyl; to purify it, it is treated with three to four times its volume of a concentrated solution of sodium bisulphite; the crystalline mass is expressed, dissolved in a small quantity of water, and decomposed with a concentrated solution of sodium carbonate—the treatment being repeated, if necessary.

It is a colorless oil, having an acrid taste and the odor of bitter almonds; sp. gr. 1.043; boils at 179.4°; soluble in thirty parts of water, and in all proportions in alcohol and ether.

Its vapor, passed through a tube filled with fragments of pumice and heated to redness, is decomposed into benzene and carbon dioxide. Oxidizing agents convert it into benzoic acid, a change which occurs by mere exposure to air. Nascent hydrogen converts it into benzylic alcohol. With chlorine or bromine it forms benzoyl chloride or bromide. Sulphuric acid dissolves it when heated, forming a purple-red color, which turns black if more strongly heated.

When *perfectly pure*, benzoic aldehyde exerts no deleterious action when taken internally; owing, however, to the difficulty of completely removing the hydrocyanic acid, the substances usually sold as *oil of bitter almonds*, *ratafia*, and *almond flavor*, are almost always poisonous, if taken in sufficient quantity. They may contain as much as ten to fifteen per cent. of hydrocyanic acid, although said to be "purified"; the presence of the poisonous substances may be detected by the tests given on page 340.

Cuminic aldehyde, $C_9H_{11}(COH)$, exists, along with a liquid hydrocarbon, in cumin-seeds and essence of cumin, from which it is obtained, by fractional distillation, in much the same way as benzoic aldehyde. It is a colorless or yellowish oil; has a penetrating and disagreeable odor, and an acrid, burning taste; sp. gr. 0.9727 at 13°; boils at 220°. Its reactions are similar to those of benzoic aldehyde.

Salicylic aldehyde—*Salicyl hydride*—*Salicylol*—*Salicylous acid*—$C_6H_4(OH)COH$—exists in the flowers of *spiræ ulmaria*, and is the principal ingredient of the essential oil of that plant. It is best obtained by oxidizing salicine (*q. v.*) with a mixture of sulphuric acid and potassium dichromate.

It is a colorless oil; turns red on exposure to air; has an agreeable, aromatic odor, and a sharp, burning taste; sp. gr. 1.173 at 13.5°; boils at 196.5°; soluble in water, more so in alcohol and ether.

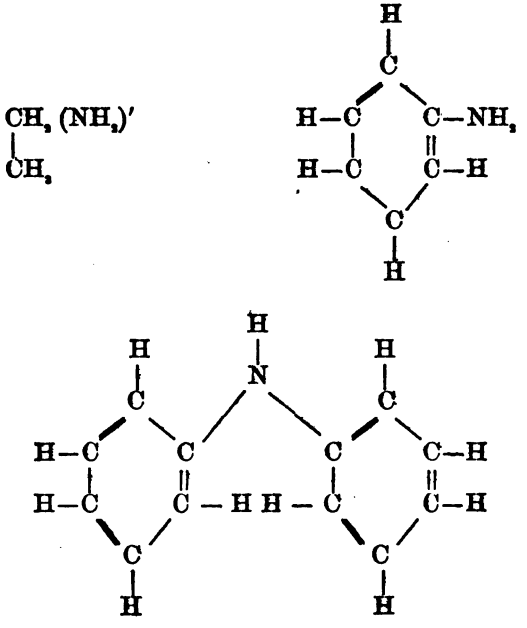
It is, as we should suspect from its origin, a substance of mixed function, possessing the characteristic properties of aldehyde and phenol. It produces a great number of derivatives, some of which have the characters of salts and ethers.

Anisic aldehyde, $C_6H_3CH_3(OH)COH$—obtained from the essence of anis; is a yellowish liquid; has an aromatic odor and a burning taste; sp. gr. 1.09 at 20°; boils at 254°; almost insoluble in water, readily soluble in alcohol and ether.

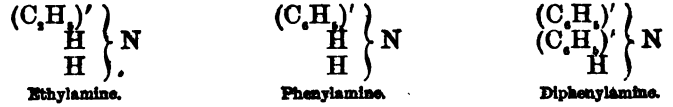
Amines.

Phenylamines.

Benzene may be considered as being made up of a radical group $(C_6H_5)'$, united to hydrogen; this radical is known as *phenyl*, and benzene is, therefor, phenyl hydride, as marsh-gas is methyl hydride. The radical, phenyl, is capable, like methyl, of replacing atoms of hydrogen of ammonia to form amines precisely similar in typical constitution to those of the univalent alcoholic radicals (see p. 155); or these amines may be considered as formed by the substitution of a group NH_2 for an atom of hydrogen of one molecule of benzene, or of $(NH)''$ for two atoms of hydrogen in two molecules, etc.:



or typically:



These amines are, in their turn, capable of forming a vast number of products of substitution, salts, etc. Of the compounds of this class, the most important by far is:

Phenylamine—*Amido-benzene—Amido-benzol—Aniline—Kyanol—Cristalline*—$\left.\begin{matrix}C_6H_5\\H_2\end{matrix}\right\}$N.—It was discovered in 1826, by Unverdorben, among the products of the dry distillation of indigo; later it was found

to exist in coal-tar; and, finally, Zinin discovered the method of obtaining it from nitro-benzene which is at present used. This reaction is a reduction, consisting in the removal of O_2, and the substitution therefor of H_2:

$$\underset{\text{Nitrobenzene.}}{C_6H_5(NO_2)} + \underset{\text{Hydrogen.}}{3H_2} = \underset{\text{Amidobenzene.}}{C_6H_5(NH_2)} + \underset{\text{Water.}}{2H_2O}$$

Aniline is now obtained in large quantities from nitrobenzene, which is mixed with acetic acid, and to the mixture iron turnings or borings are gradually added; the nascent hydrogen liberated by the action of the metal upon the acid being the reducing agent; the addition of iron is continued until a pasty mass is formed, which is then neutralized with lime and subjected to distillation.

Aniline is also formed in other reactions: in small quantity when phenol and ammonia are long heated together under pressure; by the dry distillation of indigo, etc.

When pure, aniline is a colorless liquid; has a peculiar, aromatic odor, and an acrid, burning taste; sp. gr. 1.02 at 16°; boils at 184.8°; crystallizes at −8°; soluble in thirty-one parts of cold water, soluble in all proportions in alcohol, ether, carbon disulphide, etc.; when exposed to air, it turns brown, the color of the commercial "oil," and, finally, resinifies; it is neutral in reaction.

Its vapor, when heated to redness, is decomposed into carbon, ammonia, ammonium cyanide, and a complex brown liquid. Oxidizing agents convert it into blue, violet, red, green, or black derivatives. Chlorine, bromine, and iodine act upon it violently to produce products of substitution. Concentrated sulphuric acid converts it, according to the conditions, into *sulphanilic* or *disulphanilic acid*. With acids it unites, after the manner of the ammonias, without liberation of water or hydrogen to form salts, most of which are crystallizable, soluble in water, and colorless, although by exposure to air, especially if moist, they turn red.

The presence of aniline may be detected by the following characters: 1st, on the addition of a nitrate and of sulphuric acid, a red color is produced; 2d, cold sulphuric acid does not color it *alone*, on the addition of potassium dichromate, a fine blue color is produced, which, *on dilution with water*, passes to violet, and, if not diluted, to black (see Strychnine); 3d, with calcium hypochlorite solution it gives a violet color; 4th, when heated with cupric chlorate, a deep black color is produced; 5th, a deep crimson color appears when it is heated with mercuric chloride.

Experiments upon animals show aniline to be an active poison when taken in the liquid form, or by inhalation of its vapor; its salts, however, *if pure*, seem to be without deleterious action. The symptoms produced by aniline are very similar to those of nitrobenzene poisoning.

Derivatives of aniline.—Although aniline and most of its salts are colorless, some of the most brilliant dyes at present in use are produced from them. We merely mention the more prominent:

Rosaniline chloride—fuchsine—magenta—a magnificent red dye, formerly obtained by oxidizing aniline with arsenic acid and combining the base so formed with hydrochloric acid. The difficulty of disposing of the arsenical refuse of this process, and the deleterious action of the dyes from which the arsenic had been imperfectly removed, have led to a modification of the process in which nitrobenzene itself is used as the oxidizing agent. The base, rosaniline, is an almost colorless, crystalline compound, although its salts are so brilliantly colored.

The dyes derived from rosaniline are very numerous; prominent among them are *fuchsine*, rosaniline chloride, a green, crystalline substance, soluble in alcohol, with a beautiful magenta color; *Hofmann's violet*, triethyl-rosaniline, obtained by heating together rosaniline and ethyl iodide; *Lyons blue*, triphenyl-rosaniline hydrochloride, obtained by heating rosaniline with an excess of aniline; *gas green*, obtained by heating rosaniline chloride with aldehyde and sulphuric acid; *Paris violet*, obtained by the oxidation of methyl aniline.

Mauvein is a base whose sulphate, obtained by mixing cold dilute solutions of potassium dichromate and aniline sulphate, is a fine, purple dye. A blue dye is also obtained by heating mauvein with aniline.

Aniline black is obtained by acting on aniline with a mixture of cupric sulphate and potassium chlorate.

Saffronin is a base derived from commercial oils, rich in the superior homologues of aniline (toluidines); its hydrochlorate is largely used in place of safflower for dyeing silks.

SIXTH SERIES OF HYDROCARBONS.

C_nH_{2n-8}.

This series has at present but two representatives, derivable from benzene by the substitution of one lateral chain for an atom of hydrogen.

Cinnamene—*Styrolene—Cinnamol—Styrol—Liquid essence of styrax*—C_8H_8—exists ready formed in essential oil of styrax; it is also formed by decomposition of cinnamic acid (*q. v.*), or, synthetically, by the action of a red heat upon pure acetylene, a mixture of acetylene and benzene, or a mixture of benzene and ethylene.

It is a colorless liquid; has a penetrating odor, recalling those of benzene and naphthalene, and a peppery taste; sp. gr. 0.928 at 16°; boils at 143°; soluble in all proportions in alcohol and water; neutral in reaction.

Cedrene, $C_{15}H_{24}$—is the liquid hydrocarbon of essence of Virginia cedar; it is a colorless liquid, of sp. gr. 0.984 at 14.5°, and boils at 237°.

Alcohols—Series $C_nH_{2n-8}O$.

There are but two alcohols of this series known:

Cinnyl alcohol..... $C_9H_{10}O$ | Cholesterin..... $C_{26}H_{44}O$

Cinnyl alcohol—*Cinnamic alcohol—Styrolic alcohol—Styrone—Styracone—Peruvine*—C_8H_8OH—is obtained by distilling styracine (see below) with a concentrated solution of potash or soda.

It crystallizes in soft, silky needles; has a sweet taste and an odor of hyacinth; fuses at 33°; distils at 250°; sparingly soluble in water, and readily soluble in alcohol, ether, and cinnamene.

Styracine, or *cinnyl cinnamate*, exists in Peru balsam and in styrax, from the latter of which it is obtained.

It crystallizes in prisms, grouped in bundles; odorless and tasteless; fuses at 38°; insoluble in water, sparingly soluble in cold alcohol,

readily soluble in ether. When heated with potash it is decomposed, liberating cinnamic alcohol.

Cholesteric alcohol—*Cholesterin*—$C_{26}H_{43}OH$.—This substance, of great physiological interest, is shown by its reactions to be certainly an alcohol, and probably one belonging to this series; although it is usually classed by physiologists among the fats for no better reason than that it is greasy to the touch and soluble in ether.

It has been found in the animal economy, normally in the bile, blood (especially that coming from the brain), nerve-tissue, brain, spleen, sebum, contents of the intestines, meconium and fæces; pathologically in biliary calculi, in the urine in diabetes and icterus, in the fluids of ascites, hydrocele, etc., in tubercular and cancerous deposits, in cataracts, in atheromatous degenerations, and sometimes, in masses of considerable size, in certain cerebral tumors. It has also been found to exist in the vegetable world in peas, beans, olive-oil, wheat, etc. It has not been obtained by synthesis.

Cholesterin is best obtained from biliary calculi, the lighter-colored varieties of which consist almost entirely of this substance. The calculi are pulverized, extracted with boiling ether, the solution filtered hot, the ether distilled off, the residue dissolved in boiling alcohol, and the solution allowed to cool; the crystals which separate are heated for some time with alcohol containing a little potash; on cooling, crystals form, which are finally washed with alcohol so long as the washings are colored or alkaline, and recrystallized from ether.

Cholesterin crystallizes with or without water of crystallization; from benzol, petroleum, chloroform, or anhydrous ether, it separates in delicate, colorless, silky needles, having the composition $C_{26}H_{44}O$; from hot alcohol, or a mixture of alcohol, and ether, it crystallizes in rhombic plates, usually with one obtuse angle wanting, having its composition $C_{26}H_{44}O + 1$ Aq.; these crystals, transparent at first, become opaque on exposure to air, from loss of aq. It is insoluble in water, in alkalies and dilute acids, difficultly soluble in cold alcohol, readily soluble in hot alcohol, ether, benzol, acetic acid, glycerin, and solutions of the biliary acids. It is odorless and tasteless. When anhydrous it fuses at 145° and solidifies at 137°; at 360° in vacuo it distils unchanged; sp. gr. 1.046. It is lævogyrous, $[a]_D = 31.6°$ in any solvent.

It combines readily with the volatile fatty acids. From its solution in glacial acetic acid a compound having the composition $C_{26}H_{44}O,C_2H_4O_2$ separates in fine curved crystals, which are decomposed on contact with water or alcohol; when heated with acids under pressure, it forms true ethers. Hot nitric acid oxidizes it to *cholesteric acid*, $C_8H_{10}O_5$, which is also produced by the oxidation of biliary acids; a fact which indicates the probable existence of some relation between the methods of formation of cholesterin and of the biliary acids in the economy.

Cholesterin may be recognized by the following reactions: 1st, moistened with concentrated nitric acid and evaporated to dryness, a yellow residue remains, which turns brick-red (not bright red, as in the case of uric acid) on the addition of ammonium hydrate; 2d, it is colored violet when a mixture of two volumes sulphuric or hydrochloric acid, and one volume ferric chloride solution is evaporated upon it; 3d, when ground up with sulphuric acid and chloroform added, a blue-red or violet color is produced, which passes into green on exposure to air.

Acids—Series $C_nH_{2n-10}O_2$.

Cinnamic acid, $C_6H_5,COOH$ — exists in syrax, and in Peru and Tolu balsams; it is also formed by the oxidation of cinnyl alcohol; by the action of potassium hydrate an essence of cinnamon; and by heating together acetyl chloride and benzoyl hydride under pressure.

It forms prismatic crystals; sp. gr. 1.195; fuses at 137°; boils at 293°; quite soluble in cold water and ether.

Cinnamic aldehyde, C_6H_5,COH—is one of the constituents of essence of cinnamon. It is a colorless oil; denser than water; turns brown rapidly on exposure to air, from which it also absorbs oxygen and is converted into cinnamic acid.

SEVENTH SERIES OF HYDROCARBONS.

C_nH_{2n-10}.

The only representative of this series at present known is

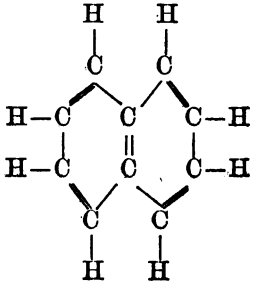
Naphthydrene—*Naphthylene hydride*—$C_{10}H_8$—a substance having only theoretical interest, obtained by heating naphthalene with potassium, and decomposing the product with water. It also occurs in heavy petroleum. It is a colorless liquid; boils at 205°, and has a strong, disagreeable odor.

EIGHTH SERIES OF HYDROCARBONS.

C_nH_{2n-12}.

The only term of this series is

Naphthalene, $C_{10}H_8$—discovered in 1820 in coal-tar. It has been formed by an interesting synthesis which indicates its constitution; benzene and ethylene, when heated together, unite to form, first, cinnamene (*q. v.*), and afterward naphthalene. It is constituted by the fusion of two benzol groups by two carbon-atoms, thus:



It is obtained in considerable quantities from coal-tar, by fractional distillation, and is used for the production of a number of brilliant dyes.

It crystallizes in large, brilliant plates; has a burning taste and a faint aromatic odor; fuses at 80° and boils at 217°, subliming, however, at a

temperature much below its boiling-point; sp. gr. 1.158 at 18°; it burns with a bright, but very smoky flame; is insoluble in cold water, very sparingly soluble in boiling water, readily soluble in alcohol, ether, and essences.

Chlorine, bromine, nitric acid, and concentrated sulphuric acid attack it to form substitution compounds. Alkalies do not affect it. Nitric acid after a time oxidizes it to phthalic acid.

Although many of the derivatives of naphthalene, which are very numerous, are of great chemical and industrial interest, they do not call for further mention here.

NINTH SERIES OF HYDROCARBONS.

$$C_nH_{2n-14}$$

Is also represented by a single hydrocarbon, derived from naphthalene.

Acenaphthalene, $C_{12}H_{10}$—is produced synthetically by continuing the heating of naphthalene with ethylene, the reaction occurring in three steps.

It also exists in coal-tar, from that portion of which, distilling at 270° —290°, it is best obtained.

It is only of theoretical interest.

TENTH SERIES OF HYDROCARBONS.

$$C_nH_{2n-16}$$

Is represented by two terms: **Fluorene**, a solid, crystalline body, boiling at 305°, obtained from coal-tar; and **Stilbene**, obtained by the action of ammonium sulphydrate upon an alcoholic solution of benzoic aldelhyde.

ELEVENTH SERIES OF HYDROCARBONS.

$$C_nH_{2n-18}$$

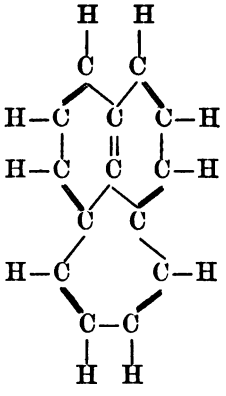
Anthracene, $C_{14}H_{10}$, is a substance which, although of but little medical interest, has assumed considerable importance in the arts and in chemical philosophy.

It exists as a constituent of coal-tar, and is obtained by expression from the substance remaining in the still after the distillation of naphthalene, etc. The commercial product thus obtained is a yellowish mass containing from fifty per cent. to eighty per cent. of anthracene, the purification of which is a matter of considerable difficulty. It has also been obtained synthetically.

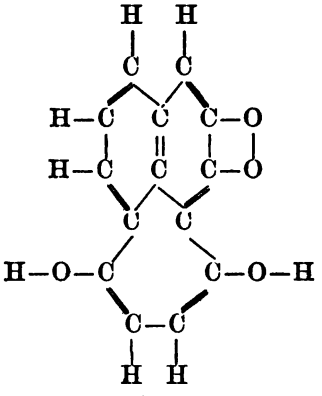
When pure, anthracene crystallizes in rhombic tables having a bluish fluorescence; fusible at 210° and boiling above 360°; its best solvents are benzene and carbon disulphide, in which, however, it is only sparingly soluble.

Anthracene forms a number of products of substitution; the only one of which we will mention is

Alizarin, $C_{14}H_8O_4$—a coloring matter now prepared on a large scale from anthracene, formerly only obtained from madder, and very extensively used in dyeing. As napthalene is formed by the condensation of two molecules of benzene, anthracene is constituted by the condensation of three; the constitution of anthracene and the relation of alizarin to it are shown by the formulæ:



Anthracene.



Alizarin.

HIGHER SERIES OF HYDROCARBONS.

The twelfth series is not at present represented. Of the thirteenth series, one hydrocarbon, *pyrene*, $C_{16}H_{10}$, is known; and one of the fourteenth series, *chrysene*, $C_{18}H_{12}$, both obtained from coal-tar; the former fusing at 142°, the latter at 230°—235°.

CYANOGEN COMPOUNDS.

The substances which we have considered are all derivable, more or less directly, from the various hydrocarbons, and may be considered, upon the theory of types, to be formed by the substitution of radicals composed of carbon and hydrogen, carbon and oxygen, or carbon, hydrogen and oxygen, for atoms of hydrogen of the three typical substances, hydrogen, water, and ammonia. There are a number of very important substances which are typically considered as containing the radical $(CN)'$, which radical, known as *cyanogen*, possesses the same power of passing unchanged from compound to compound, as do methyl and ethyl, like which, also, it is incapable of separate existence. The substance sometimes known as cyanogen is not CN, but

Dicyanogen $(CN)_2$.

This body is prepared by heating mercury cyanide in a small retort and collecting the gaseous product over mercury.

Dicyanogen is a colorless gas, has a pronounced odor of bitter almonds; under a pressure of 4 atm. at 25° it is liquefied; sp. gr. 1.8064 A.;

it burns in air with a purple flame, giving off nitrogen and carbon dioxide.

It is quite soluble in water; the solution on exposure to air turns brown; with water alone, or with water and ammonia, dicyanogen enters into combinations which show the relations existing between the cyanogen compounds and others previously considered:

$$\underset{\text{Dicyanogen.}}{(CN)_2} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Ammonium oxalate.}}{C_2O_4(NH_4)_2}$$

$$\underset{\text{Dicyanogen.}}{(CN)_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Cyanic acid.}}{CNOH} + \underset{\text{Hydrocyanic acid.}}{CNH}$$

$$\underset{\text{Cyanic acid.}}{CNOH} + \underset{\text{Water.}}{H_2O} = \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Carbon dioxide.}}{CO_2}$$

$$\underset{\text{Cyanic acid.}}{CNOH} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Urea.}}{CON_2H_4}$$

It has a very deleterious action upon both animal and vegetable life, even when largely diluted with air.

Hydrogen Cyanide.

Cyanogen hydride—Hydrocyanic acid—Prussic acid—$\left.\begin{matrix}CN\\H\end{matrix}\right\}$—exists ready formed in the juice of *cassava*, and is formed by the action of water upon bitter almonds, cherry-laurel leaves, etc. It is also formed in a great number of reactions: by the passage of the electric discharge through a mixture of acetylene and nitrogen; by the action of chloroform on ammonia; by the distillation or the action of nitric acid upon many organic substances; by the decomposition of cyanides.

It is always prepared by the decomposition of a cyanide, although the nature of the cyanide and of the decomposing agent differ in the process advised by different authors, and according as the product is required pure or in dilute solution. Its preparation in the pure form is an operation attended with the most serious danger, and should only be attempted by those well trained in chemical manipulation. For medical uses a very dilute acid is required; the *acid. dil. hydrocyanicum* (U. S., Br.) contains, if freshly and properly prepared, two per cent. of anhydrous acid; that of the French Codex is much stronger—ten per cent.

The pure acid is a colorless, mobile liquid, has a penetrating and characteristic odor; sp. gr. 0.7058 at 7°; crystallizes at −15°; boils at 26.5°; is rapidly decomposed by exposure to light. The dilute acid of the United States Pharmacopœia is a colorless liquid, having the odor of the acid; faintly acid, the reddened litmus returning to blue on exposure to air; sp. gr. 0.997; ten grams of the acid should be accurately neutralized by 1.27 grams of silver nitrate. The dilute acid deteriorates on exposure to light, although more slowly than the concentrated; a trace of phosphoric acid added to the solution retards the decomposition.

An acid of the medicinal strength may be obtained extemporaneously from argentic cyanide (*q. v.*); 9.925 grams of the pure, dry, salt are added to a mixture of 8.3 grams of hydrochloric acid of sp. gr. 1.16 made up to 98 c.c., with distilled water; the resulting liquid, after agitation, is filtered from the precipitated silver chloride. A disadvantage of this method

is that while an excess of silver nitrate is undesirable, an excess of hydrochloric acid rapidly decomposes hydrocyanic acid, with formation of ammonium chloride and formic acid; the neutralization must therefor be most accurate, a result not readily attained in practice. The acid known as *Scheele's* contains five per cent. of true acid.

Most powerful acids decompose hydrocyanic acid quickly; the alkalies enter into double decomposition with it to form *cyanides;* chlorine and bromine decompose it, with formation of cyanogen chloride and bromide; nascent hydrogen converts it into methylamine.

The presence of hydrocyanic acid or of a soluble cyanide is recognized by the following characters: 1st, with silver nitrate a dense, white precipitate is formed; the precipitate is not redissolved on the addition to the liquid of a small quantity of nitric acid, but is dissolved if separated and heated with concentrated nitric acid; it is but sparingly soluble in ammonia; freely soluble in solutions of alkaline cyanides or hyposulphites. 2d, when treated with a solution of ammonium sulphydrate, and a solution of ferric chloride added, a blood-red color is produced. 3d, on the addition of potassium hydrate, and subsequently of a mixture of ferrous and ferric sulphates, a greenish precipitate is formed, which is partly redissolved by hydrochloric acid, leaving a deep blue color. 4th, a dilute solution of picric acid produces a blood-red color when heated with a cyanide and subsequently cooled.

Toxicology.—Hydrocyanic acid is a violent poison, whether it be inhaled as vapor or swallowed, either in the form of dilute acid, of soluble cyanide, or of the pharmaceutical preparations containing it, such as oil of bitter almonds and cherry-laurel water, its action being more rapid when taken by inhalation or in aqueous solution than in other forms. When the medicinal acid is taken in poisonous dose, its lethal effect may seem to be produced instantaneously; nevertheless, several respiratory efforts usually are made after the victim seems to be dead, and instances are not wanting in which there was time for considerable voluntary motion between the time of the ingestion of the poison and unconsciousness. In the great majority of cases the patient is either dead or fully under the influence of the poison on the arrival of the physician, who should, however, not neglect to apply the proper remedies if the faintest spark of life remain. Chemical antidotes are, owing to the rapidity of action of the poison, of no avail, although possibly chlorine, recommended as an antidote by many, may have a chemical action on that portion of the acid already absorbed. The treatment indicated is directed to the maintenance of respiration; cold douche, galvanism, artificial respiration until elimination has removed the poison. If the patient survive an hour after taking the poison, the prognosis becomes very favorable; in the first stages it is exceedingly unfavorable, unless the quantity taken has been very small.

In cases of death from hydrocyanic acid a marked odor of the poison is almost always observed in the apartment and upon opening the body, even several days after death. In cases of suicide or accident, the vessel from which the poison has been taken will usually be found in close proximity to the body, although the absence of such vessel is *not* proof that the case is one of homicide.

The presence of hydrocyanic acid may be readily detected in the body after death, and, notwithstanding the volatility and instability of the poison, its presence has been detected two months after death, although the chances of separating it are certainly the better the sooner after death the analysis is made. The search for hydrocyanic acid is combined

with that for phosphorus (see p. 109); the part of the distillate containing the more volatile products is examined by the tests given above; it is best, when the presence of free hydrocyanic acid is suspected, to distil at first without acidulating; *in such cases the stomach should never be opened until immediately before the analysis.*

Cyanic Acid.

Cyanogen hydrate, $\overset{CN}{H}\!\!>\!O$—does not exist in nature; it is obtained by calcining the cyanides in presence of an oxidizing agent; or by the action of dicyanogen upon solutions of the alkalies or alkaline carbonates; the best method of obtaining it is by the distillation of cyanuric acid.

It is a colorless liquid; has a strong odor, resembling that of formic acid; its vapor is irritating to the eyes, and it produces vesication when applied to the skin; it is soluble in water. When free it is readily changed by exposure to air into cyamelide. The acid itself is of little interest; some of its salts and ethers, however, are of industrial importance.

Sulphocyanic Acid.

Cyanogen sulphydrate, $\overset{CN}{H}\!\!>\!S$—bears the same relation to cyanic acid that carbon disulphide does to carbon dioxide. It is obtained by the decomposition of its salts, which are obtained by boiling a solution of the cyanide with sulphur, by the action of dicyanogen upon the metallic sulphide, and in several other ways.

The free acid is a colorless liquid; crystallizes at −12.5°; boils at 102.5°; acid in reaction; sp. gr. 1.040 at 17°. The prominent reaction of the acid and of its salts is the production of a deep red color with the ferric salts; the color being discharged by solution of mercuric chloride, but not by hydrochloric acid.

Sulphocyanic acid exists in human saliva in combination, probably, with sodium. The free acid is actively poisonous and its salts were formerly supposed to be so also; it is probable, however, that much of the deleterious action of the potassium salt—that usually experimented with—is due as much to the metal as to the acid.

Metallocyanides.

The radical cyanogen, besides combining with metallic elements to form true cyanides, in which the radical (CN) enters as a univalent atom, is capable of combining with certain metals; notably those of the iron and platinum groups, to form still more complex radicals, which, combining with hydrogen, form acids, and with basic elements form salts in which the analytical reactions of the metallic element entering into the radical, are completely masked. Of these *metallocyanides* the best known are those in which iron enters into the radical. As iron is capable of forming two series of compounds, in one of which the single atom Fe″ enters in its divalent capacity, and in the other of which the hexavalent

double atom $(Fe_2)^{VI}$ is contained; so, uniting with cyanogen, iron forms two ferrocyanogen radicals: $[(CN)'_6Fe'']^{IV}$, ferrocyanogen, and $[(CN)'_{12}(Fe_2)^{VI}]^{VI}$, ferricyanogen, each of which unites with hydrogen to form an acid, corresponding to which are numerous salts: $(C_6N_6Fe)H_4$, *hydroferrocyanic acid*, tetrabasic; and $(C_{12}N_{12}Fe_2)H_6$, *hydroferricyanic acid*, hexabasic (see potassium and iron salts).

COMPOUNDS OF UNKNOWN CONSTITUTION.

Glucosides.

Under this head are classed a number of substances, some of them important medicinal agents, which are the products of vegetable or animal nature; their characteristic property is that, under the influence of a dilute mineral acid, they yield glucose, phloroglucine or mannite, together with some other substance. Under the supposition that glucose and its congeners are alcohols, it is quite probable that the glucosides are their corresponding ethers.

Some of the more important glucosides are treated of below in alphabetical order:

Amygdalin, $C_{20}H_{27}NO_{11}$, exists in cherry-laurel and in bitter almonds, but not in sweet almonds. Its characteristic reaction is that, in the presence of *emulsin*, which exists in sweet as well as in bitter almonds, and of water, it is decomposed into glucose, benzoic aldehyde, and hydrocyanic acid.

The same reaction is brought about by boiling with dilute sulphuric or hydrochloric acids. Bitter almonds contain about two per cent. of amygdalin.

Apiïn, $C_{24}H_{28}O_{13}$, is a glucoside obtained from parsley. Dilute acids decompose it into a white, flocculent substance of unknown composition, and a non-fermentable, uncrystallizable sugar.

Arbutin, $C_{12}H_{16}O_7$(?)—a glucoside supposed to be the active principle of *uva ursi*, is a bitter, crystalline substance, very soluble in water, decomposed by emulsin or by dilute acids into glucose and hydroquinon.

Carminic acid, $C_{17}H_{18}O_{10}$, is the red coloring matter of cochenil; dilute sulphuric acid decomposes it into a non-fermentable sugar and a new red pigment, insoluble in ether, but soluble in alcohol.

Cathartic acid—a bitter, uncrystallizable glucoside, obtained from senna.

Chitin is an animal product, and forms the organic basis of the tissues of insects, spiders, and crustaceans. It withstands the action of reagents well, but, when boiled with dilute sulphuric acid, yields ammonia, a fermentable sugar, and a substance which appears to be lactamide.

Colocynthin—a very bitter and actively purgative glucoside, obtained from colocynth, soluble in water and alcohol; decomposed by dilute acids into a resin, *colocynthein*, and glucose.

Crocin—a yellowish red glucoside obtained from saffron; soluble in alcohol; decomposed into *crocetin* and a sugar resembling, but not identical with, glucose.

Digitalin.—The substance known until recently as digitalin was an uncrystallizable material, soluble in water, obtained from *digitalis*, whose medicinal properties it possessed to a high degree. More recent researches have, however, shown that this substance, although very active,

does not contain all the active principles of the plant, which contains the true glucoside as a crystalline substance, *insoluble in water*, but soluble in alcohol. By a complicated system of extraction by water and by alcohol, and decolorization and purification of the extracts, Nativelle has obtained from all parts of the plant, except the seeds, 1st, a gummy, uncrystallizable, white substance, soluble in water, sparingly soluble in alcohol; very bitter, acrid, and irritating, which he calls *amorphous digitaleine;* 2d, the true glucoside, *insoluble digitalin*, which crystallizes in fine needles, almost insoluble in water, readily soluble in alcohol; intensely and persistently bitter, and actively poisonous. Sulphuric acid dissolves it with a greenish brown color, changing to red under the influence of bromine vapor, and to emerald green on subsequent dilution with water. Hydrochloric acid of 20° strength dissolves it, the solution assuming in a few moments a fine green color. When suspended in water and treated with sulphuric acid it is entirely decomposed, with production of glucose and a peculiar substance, *digitaliretin*, $C_{15}H_{25}O_5$. Digitalis also contains a white, insipid crystalline substance, insoluble in water—*digitalose*, and a crystallizable acid—*digitalic acid*, very soluble in water and in alcohol; very prone to decomposition when exposed to light; acid in taste and in reaction.

For the detection of digitalin in cases of poisoning, see p. 348.

Glycyrrhizin—a non-crystallizable, yellowish, pulverulent principle, obtained from liquorice; soluble with difficulty in cold water, soluble in hot water, alcohol, and ether; bitter-sweet in taste. By long boiling with dilute acids it is decomposed into glucose and *glycyrrhetin*, $C_{18}H_{26}O_4$.

Jalapin, $C_{34}H_{56}O_{16}$, is the active principle of scammony, and exists also to a limited extent in jalap (see below). It is an insipid, colorless, amorphous substance, which is decomposed by dilute acids into glucose and *jalapinol*. The active ingredient of jalap is not, as the name would imply, jalapine, but a resinous substance called *convolvulin*, which is insoluble in ether, odorless, and insipid. It is not attacked by dilute sulphuric acid, although the concentrated acid dissolves it with a carmine-red color, slowly turning to brown; in alcoholic solution it is decomposed by gaseous hydrochloric acid into glucose and *convolvulinic acid*. It is an active purgative agent.

Phlorizin, $C_{21}H_{24}O_{10}$, is a glucoside obtained from the bark of apple-, plum-, pear-trees, etc.; it crystallizes is silky needles; sparingly solub e in cold water, very soluble in hot water and in alcohol. Is colored yellow, then brown, by sulphuric acid; dilute acids decompose it into glucose and *phloretin*, $C_{16}H_{14}O_5$.

Quercitrin, or *quercitric acid*—obtained from black-oak bark; crystallizes in rectangular or rhombic plates; neutral; odorless; bitter; almost insoluble in cold water; soluble in hot water and in alcohol; readily soluble in alkaline solutions, with a greenish yellow color, turning to brown by oxidation on exposure to air. Dilute mineral acids decompose it into *isodulcite*, $C_6H_{14}O_6$, and *quercetin*, $C_{27}H_{18}O_{12}$.

Quinovin, or *quinovatic acid*, a bitter principle, possessed of acid functions, obtained from the false bark known as *cinchona nova;* it is a glucoside, being decomposed by dilute acids into a sugar resembling mannitan and *quinovic acid*.

Salicin, $C_{13}H_{18}O_7$—one of the best known of the glucosides; derives its name from its chief source, the bark of the willow (*salix*). It is a white, crystalline substance; insoluble in ether, soluble in water and in alcohol; fuses at 120°, and is decomposed at a temperature above 200°; it is very bitter; its solutions are dextrogyrous, $[a]_D = 55.8°$. Dilute acids

decompose it into glucose and *saligenin* (*q. v.*). Concentrated sulphuric acid colors it red, the color being discharged on the addition of water. When taken into the economy it is converted into salicylic aldehyde and acid, which are eliminated in the urine.

Santonin—*Santonic acid*—$C_{15}H_{18}O_3$—*Santoninum* (U. S., Br.)—a glucoside having distinct acid properties; obtained from various species of *Artemisia* (Levant worm-seed). It crystallizes in colorless, rectangular prisms, which turn yellow on exposure to light; odorless and tasteless; insoluble in cold water, sparingly soluble in hot water, alcohol, and ether; its solutions are faintly acid in reaction. Sulphuric acid, aided by heat, decomposes it into glucose and a yellowish, odorless, tasteless resinoid, insoluble in water, soluble in alcohol, called *santoniretin*. Santonin, in solution, gives a chamois-colored precipitate with the ferric salts, and a white precipitate with silver, zinc, and mercurous salts; no precipitate with mercuric salts.

Patients taking santonin pass urine having the appearance of that containing bile, which, when treated with potash, turns cherry-red or crimson, the color being discharged by an acid, and regenerated on neutralization.

Solanin—a glucoside, having basic properties, existing in different plants of the genus *Solanum*. It crystallizes in fine, white, silky needles; having an acrid, bitter taste; insoluble in water, and but sparingly soluble in ether and in alcohol. By the action of hot dilute acids it is decomposed into glucose and a basic substance, *solanidine;* when not heated, solanin combines with acids to form uncrystallizable salts. Cold, concentrated sulphuric acid colors it orange-yellow, and finally forms with it a brown solution; nitric acid dissolves it, the solution being at first colorless, afterward rose-pink.

Tannin—Tannic acid—$C_{14}H_{10}O_9$.—Quite a number of different substances of vegetable origin, principally derived from barks, leaves, and seeds. They are amorphous, soluble in water, astringent, capable of precipitating albumen and of forming imputrescible compounds with the gelatinoids. They are, with one possible exception, glucosides. The principal varieties are the following:

Gallo-tannic acid—Acidum tannicum (U. S., Br.)—is the best known of the tannins, and is obtained from nut-galls, *galla* (U. S., Br.), which are excrescences produced upon oak-trees by the puncture of minute insects. It appears as a yellowish, amorphous, odorless, friable mass; has an astringent taste; very soluble in water, less so in alcohol, almost insoluble in ether; its solutions are acid in reaction, and on contact with animal tissues give up the dissolved tannin, which becomes fixed by the tissue to form a tough, insoluble, and non-putrescible material (leather).

Solutions of gallo-tannic acid yield insoluble precipitates with sulphuric, hydrochloric, phosphoric, and arsenic acids, sodium chloride, potassium acetate, gelatin, and ammonium chloride. It also precipitates solutions of most of the metallic salts, in many instances effecting a reduction and separation of the metallic element. The tannates of the alkaline metals are soluble, and become colored on exposure to air; almost all other tannates are insoluble, including those of the vegetable alkaloids.

A freshly prepared solution of pure gallo-tannic acid gives a dark blue precipitate with ferric salts, but not with ferrous salts. If, however, the solution have been exposed to the air, it is altered by oxidation, and gives, with ferrous salts, a black color, in whose production gallic acid probably plays an important part, which is the coloring material of ordinary writing-

ink. A good ink is made by boiling six parts of crushed nut-galls in forty-five parts (by weight) of water for three hours, replacing the water as it evaporates, cooling and filtering; a solution containing 2.5 parts of gum arabic dissolved in a small quantity of water and strained, and, finally, a concentrated solution of 2.5 parts of ferrous sulphate, are added; the mixture is exposed to the air until it has assumed the proper tint (two to three weeks), decanted, and bottled. The color of this ink is discharged by oxalic and sulphuric acids. Removals of writing in iron ink by acids may be detected by first moistening with pure water, and testing by litmus paper; the reaction will be acid, unless the acid have been neutralized; the surface is then pencilled with a dilute solution of ammonia, and afterward with a solution of nut-galls, when the writing will become more or less plainly visible.

Other characters of gallo-tannic acid are the formation of precipitates with solutions of albuminoids, gelatin, alkaloids, and tartar emetic. Its watery solution remains unaltered when protected from air, but by exposure it becomes colored and mouldy, ferments, and is converted into gallic acid; the same changes are caused by dilute acids and in the economy when gallo-tannic acid is ingested.

Although formerly considered as a glucoside, and, in all probability, existing as such in vegetable nature, recent researches have shown gallo-tannic acid to be, not a glucoside, but *digallic acid.*

Caffetannic acid exists in saline combination in coffee and in Paraguay tea. It colors the ferric salts green, and does not affect the ferrous salts, except in the presence of ammonia; it precipitates the salts of quinine and of cinchonine, but does not precipitate tartar emetic or gelatin. It is a glucoside, being decomposed by suitable means into *caffeic acid* and mannitan.

Cachoutannic acid, obtained from catechu, is soluble in water, alcohol, and ether. Its solutions precipitate gelatin, but not tartar emetic; they color the ferric salts grayish green.

Morintannic acid—Maclurin—a yellow, crystalline substance, obtained from fustic; more soluble in alcohol than in water. Its solutions precipitate green with ferroso-ferric solutions; yellow with lead acetate; brown with tartar emetic; yellowish brown with cupric sulphate. It is decomposable into phloroglucin and *protocatechuic acid.*

Quercitannic acid is the active tanning principle of oak-bark; it differs from gallo-tannic acid in not being capable of conversion into gallic acid, and in not furnishing pyrogallol on dry distillation. It forms a violet-black precipitate with ferric salts. The tannin existing in black tea seems to be quercitannic acid.

Quinotannic acid, a tannin existing in cinchona barks, probably in combination with the alkaloids. It is a light yellow substance; soluble in water, alcohol, and ether; its taste is astringent, but not bitter. Dilute sulphuric acid decomposes it, at a boiling temperature, into glucose and a red substance—*quinova red.*

The tannin existing in wines, especially in new red wines, appears to be a mixture of at least two tannins, one derived from the seeds and stems of the grape (none exists in the juice), and the other from the wood of the cask; it has the valuable property of forming an insoluble compound with albumen, and thus removes and prevents further change of the albuminoids.

NATURAL ALKALOIDS.

Under this head are classed a number of substances of great interest to the physician. They exist for the most part in vegetable nature, combined with acids, for which reason they are sometimes called *vegetable bases*, or *vegetable alkalies;* the comparatively recent discovery, however, of substances possessing all the characteristics of alkaloids in materials of animal origin, renders these terms inapplicable.

The alkaloids, as the name implies, bear some resemblance to the alkalies; they are alkaline in reaction, and combine with acids to form salts in the same way as does ammonia; there is good reason for believing, also, that these salts, as those of the amines (*q. v.*), are compounds of radicals bearing the same relation to the alkaloid itself that ammonium bears to ammonia:

$$\underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Sulphuric acid.}}{SO_4H_2} = \underset{\text{Ammonium sulphate.}}{SO_4(NH_4)_2}$$

$$\underset{\text{Morphia.}}{2C_{17}H_{19}NO_3} + \underset{\text{Sulphuric acid.}}{SO_4H_2} = \underset{\text{Morphonium sulphate.}}{SO_4(C_{17}H_{20}NO_3)_2}$$

They may be divided into two principal groups; those of the first are liquid and volatile, and are composed of carbon, hydrogen, and nitrogen; the synthesis of one of their number, effected by Schiff, leaves no doubt that they are true *amines.* The members of the second group are solid, volatilizable with difficulty, if at all, and are composed of carbon, hydrogen, nitrogen, and oxygen. Although, in spite of much patient research, no chemist has hitherto succeeded in effecting the synthesis of an oxygenated alkaloid, their compounds and the products of their decomposition lead us to believe it highly probable that they will be found to be amides. The solid alkaloids are all colorless, bitter, insoluble, or sparingly soluble in water, and most of them crystallize readily and perfectly.

A knowledge of certain physical and chemical properties possessed in varying degrees by the alkaloids in common, is of great value in pharmaceutical and toxicological chemistry.

Solubility.—As a rule the alkaloids are insoluble in water, or nearly so, more soluble in alcohol, chloroform, petroleum ether, and benzene; the solubility of the salts of the alkaloids differs in a remarkable way from that of the alkaloids themselves, for, while both are soluble in alcohol, the salts are, for the most part, soluble in water and the alkaloids are not; on the other hand, the alkaloids are soluble in petroleum ether, benzene, ether, chloroform, and amyl alcohol, in which menstrua their salts are either insoluble or very sparingly soluble. It is upon these differences of solubility that the methods for separating alkaloids, etc., from animal tissues are based (see below).

Rotary power.—All the natural alkaloids exert a rotary action upon polarized light, and all, with the exception of cinchonine and quinidine, are lævogyrous. As a rule, their rotary action is diminished by combination with an acid, in the absence of an excess of acid; with quinine, however, the reverse is the case; narcotine, when free, is lævogyrous, but in its salts is dextrogyrous.

The rotary powers of the principal alkaloids are the following:

Quinine	[a]	= −126.7°	Codeine	[a]	= −118.2°
Quinidine	[a]	+250.75°	Narceine	[a]	− 6.7°
Cinchonine	[a]	+190.4°	Strychnine	[a]	−132.07°
Cinchonidine	[a]	−144.61°	Brucine	[a]	− 61.27°
Morphine	[a]	− 88.04°	Nicotine	[a]	− 93.5°
Narcotine	[a]	−103.5°			

General reactions.—Potash, soda, ammonia, lime, baryta, and magnesia precipitate the alkaloids from solutions of their salts.

Quite a number of reagents have been suggested by various authors, which give with solutions of the salts of all the alkaloids, even when very dilute, characteristic precipitates. The principal of these reagents are:

Phosphomolybdic acid.—The reagent is prepared as follows: ammonium molybdate is dissolved in water; the solution filtered, and a quantity of crystallized hydrodisodic phosphate, one-fifth in weight of the molybdate used, is added, and then nitric acid to strong acid reaction; the mixture is warmed and set aside for a day or more. The yellow precipitate is collected on a filter, washed with water, acidulated with nitric acid, and, while still moist, transferred to a porcelain capsule, to which the liquid obtained by exhausting the remainder on the filter with ammonium hydrate is added. The fluid so obtained is warmed and gradually treated with pulverized sodium carbonate until a colorless solution is obtained; this is evaporated to dryness, a few crystals of sodium nitrate are added to the residue, and the whole gradually heated to quiet fusion, and until the ammonia has been expelled. After cooling, the residue is dissolved in warm water in the proportion of one to ten, acidulated with nitric acid, and decanted.

To use the reagent, a drop of the suspected solution is placed upon a glass plate with a black background, and near it a drop of the reagent; the two drops are then made to mix slowly by a pointed glass rod. In the presence of even a minute trace of an alkaloid (or of certain other substances) a precipitate is formed, which is bright yellow and flocculent with aniline, morphine, veratrine, aconitine, emetine, atropine, hyoscyamine; bright yellow and voluminous with theine, theobromine, coniine, nicotine; brownish yellow with narcotine, codeine, piperine; yellowish white with quinine, cinchonine, strychnine; yolk-yellow with brucine.

The value of this reagent is not in its capacity to differentiate between the various alkaloids, but in its indication of the *probable* presence or certain absence of *some* alkaloid in appreciable quantity.

Potassium iodhydrargyrate, obtained by dissolving 13.546 grams of mercuric chloride and 49.8 grams of potassium iodide in a litre of water. A very sensitive reagent when applied to alkaloidal solutions which are either acid, neutral, or very faintly alkaline in reaction.

The solution, made of the above strength, may be used for quantitative determinations. The reagent is added from a burette to the solution of alkaloid until a drop, filtered from the solution which is being tested, and placed upon a black surface, gives no precipitate with a drop of the reagent. Each c.c. of reagent used indicates the presence in the volume of liquid tested of the following quantities of alkaloids, in grams:

Aconitine	0.0267	Brucine	0.0233	Nicotine	0.00405
Atropine	0.0145	Veratrine	0.0269	Quinine	0.0108
Narcotine	0.0213	Morphine	0.0200	Cinchonine	0.0102
Strychnine	0.0167	Coniine	0.00416	Quinidine	0.0120

Of course, the process can be used only in a solution containing a single alkaloid.

Separation of alkaloids from organic mixtures and from each other.—One of the most difficult of the toxicologist's tasks is the separation from a mixture of organic material (contents of stomach, viscera) of an alkaloid in such a state of purity as to render its identification perfect. The difficulty is the greater if the amount present be small, as is usually the case; and if the search be not confined to a single alkaloid, as frequently occurs. Some of these substances, as strychnine, are detectable with much greater facility and certainty than others.

Of the processes hitherto suggested, the best is that of Dragendorff (Gerichtl. Chem. Ermittel. der Gifte, p. 141, 1876), it having been devised for the detection of any alkaloid or poisonous organic principle present in the substances examined, is very exhaustive, and well adapted to cases frequently arising in chemico-legal practice; but, on the other hand, is too intricate to be serviceable to the general practitioner.

An abridgment of this process may be of use to detect the presence of the more commonly used alkaloids in a mixture of organic material. The physician should, however, bear in mind that, in cases liable to give rise to legal proceedings, these may become seriously complicated by the analysis of any parts of the body, dejecta, or suspected articles of food, etc., by any process open to attack by the most searching cross-examination.

The substances to be examined are reduced to a fine state of subdivision, and are digested for an hour or more in water acidulated with sulphuric acid, at a temperature of 40° to 50°; this is repeated three times, the liquid being filtered and the solid material expressed. The united extracts are evaporated at the temperature of the water-bath to a *thin* syrup; this is mixed with three or four volumes of alcohol, the mixture kept at about 35° for twenty-four hours, cooled well and filtered; the residue being washed with seventy per cent. alcohol. The alcohol is distilled from the filtrate, and the watery residue diluted with water and filtered.

The filtrate so obtained contains the sulphates of the alkaloids, and from it the alkaloids themselves are separated by the following steps:

First.—The acid watery liquid is shaken with freshly rectified petroleum ether (which should boil at about 65°—70°, and should be used with caution, as it is very inflammable); after several agitations the ether layer is allowed to separate and is removed; this treatment is repeated so long as the ether dissolves anything. The residue obtained by the evaporation of the ether—*Residue* I.—is mostly composed of coloring matters, etc., which it is desirable to remove.

Second.—The same treatment of the watery liquid is repeated with benzene, which on evaporation yields *Residue* II., which is, if crystalline, to be tested for cantharidin, santonin, and digitalin (*q. v.*); if amorphous, for elaterin and colchicin.

Third.—The acid, aqueous fluid is then treated in the same way with chloroform, to obtain *Residue* III., which is examined for cinchonine, digitalin, and picrotoxin by the proper tests.

Fourth.—The watery fluid, after one more shaking with petroleum ether and removal of the ethereal layer, is rendered alkaline with ammonium hydrate and shaken with petroleum ether at 40°, the ethereal layer being removed as quickly as possible while still warm; this is repeated two or three times, and repeated with *cold* petroleum ether, which is re-

moved after a time. The warm ethereal layers yield *Residue* IV*a;* the cold ones *Residue* IV*b*. The former is tested for strychnine, quinine, brucine, veratrine; the latter for coniïne and nicotine.

Fifth.—The alkaline, watery fluid is shaken with benzene, which, on evaporation, yields *Residue* V., which may contain strychnine, brucine, quinine, cinchonine, atropine, hyoscyamine, physostigmine, aconitine, codeine, thebaine, and narceine.

Sixth.—A similar treatment with chloroform yields *Residue* VI., which may contain a trace of morphine.

Seventh.—The alkaline liquid is then shaken with amyl alcohol, which is separated and evaporated; *Residue* VII. is tested for morphine, solanin and salicin.

Eighth.—Finally, the watery liquid is itself evaporated with pounded glass, the residue extracted with chloroform, and *Residue* VIII., left by the evaporation of the chloroform, tested for curarine.

Volatile Alkaloids.

Coniïne—*Conicine*—*Cicutine*—$C_8H_{15}N$—was discovered in 1827, and is obtained from *Conium maculatum*, in which it is accompanied by two other alkaloids, *methyl-coniïne*, $C_8H_{14}N(CH_3)$, and *conhydrin*, $C_8H_{17}NO$—the former a volatile liquid, the second a crystalline solid.

Coniïne is a colorless, oily liquid; has an acid taste and a disagreeable penetrating odor; sp. gr. 0.878; can be distilled when protected from air; boils at 212°; exposed to air it resinifies; it is very sparingly soluble in water, but is more soluble in cold than in hot water; soluble in all proportions in alcohol, soluble in six volumes of ether, very soluble in fixed and volatile oils.

The vapor which it gives off at ordinary temperatures forms a white cloud when it comes in contact with a glass rod moistened with hydrochloric acid, as does ammonia. It forms salts which crystallize with difficulty. Chlorine and bromine combine with it to form crystallizable compounds; iodine in alcoholic solution forms a brown precipitate in alcoholic solutions of coniïne, which is soluble without color in an excess. Oxidizing agents attack coniïne with production of butyric acid (see below). The iodides of ethyl and methyl combine with coniïne to form iodides of ethyl and methyl-conium. It has been obtained synthetically by first allowing butyric aldehyde and an alcoholic solution of ammonia to remain some months in contact at 30°, when dibutyraldine is formed.

$$\underset{\text{Butyric aldehyde.}}{2(C_4H_8O)} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Dibutyraldine.}}{C_8H_{17}NO} + \underset{\text{Water.}}{H_2O}$$

The dibutyraldine thus obtained is then heated under pressure to 150°—180°, when it loses water:

$$\underset{\text{Dibutyraldine.}}{C_8H_{17}NO} = \underset{\text{Coniïne.}}{C_8H_{15}N} + \underset{\text{Water.}}{H_2O}$$

A synthesis which, in connection with the decompositions of coniïne, shows its rational formula to be $\left.\begin{matrix}(C_4H_7)'\\(C_4H_7)'\\H\end{matrix}\right\}N$.

The characteristic reactions of coniïne are: 1st, treated with dry hydrochloric acid gas it turns reddish purple and then deep indigo-blue; the aqueous acid of sp. gr. 1.12, when evaporated from coniïne leaves a greenish blue, crystalline mass; 2d, iodic acid forms a white precipitate in alcoholic solutions of coniïne; 3d, with sulphuric acid it forms a sulphate which by evaporation of the acid turns red and then green, giving off an odor of butyric acid.

When taken internally it is an active poison, causing death by asphyxia, often as quickly as prussic acid.

Nicotine, $C_{10}H_{14}N_2$—exists in tobacco in different proportion in different varieties, from two per cent. to eight per cent.

It is a colorless, oily liquid, which turns brown on exposure to light and air; has a burning, caustic taste and a disagreeable, penetrating odor; it distils at 250°; it burns with a luminous flame; sp. gr. 1.027 at 15°; it is very soluble in water, alcohol, the fatty oils, and ether; the last-named fluid removes it from its aqueous solution when the two are shaken together; it absorbs water rapidly from moist air. Its salts are deliquescent and crystallize with difficulty.

Its principal reactions are: 1st, an ethereal solution of iodine added to an ethereal solution of nicotine separates at first a reddish brown, resinoid oil, which gradually becomes crystalline, and there separate from the solution crystalline needles, often one to two inches long, which are ruby red by transmitted, and dark blue by reflected light; 2d, it turns violet when heated with hydrochloric acid; 3d, it is colored orange-yellow by nitric acid.

Nicotine is an active poison, being fatal to dogs in doses of 2—3 drops, by causing asphyxia. It is interesting in the history of toxicology as having been used in a case of criminal poisoning, for the investigation of which Stas devised the first systematic method of searching for the alkaloids.

Fixed Alkaloids.

These are much more numerous than those which are volatile, and form the active principles of a great number of poisonous plants. As we are yet in the dark as to the constitution of these bodies, the only classification which we can adopt is the temporary one based upon the botanic characters of the plants from which they are derived.

Opium Alkaloids.

Opium is the inspissated juice of the capsules of the poppy. It is of exceedingly complex composition, and contains, besides a neutral body called *meconine*, probably a polyatomic alcohol, $C_{10}H_{10}O_4$, a peculiar acid, *meconic acid* (*q. v.*), lactic acid, gum, albumen, wax, and a volatile matter—no less than eighteen different alkaloids, one or two of which, however, are probably formed during the processes of extraction, and do not pre-exist in opium.

The following is a list of the constituents of opium, those marked * being of medical interest:

Name.	Formula.	Percent. in Smyrna opium.	Percent. in Constantinople opium.	Name.	Formula.	Percent. in Smyrna opium.	Percent. in Constantinople opium.
*Meconic acid..	$C_7H_4O_7$	4.70	4.38	Laudanine	$C_{20}H_{25}NO_4$	....	....
Lactic acid.....	$C_3H_6O_3$	1.25	....	Papaverine.....	$C_{21}H_{21}NO_4$	1.00	....
Meconine	$C_{10}H_{10}O_4$	0.08	0.30	Opianine.....	$C_{21}H_{21}NO_7$	....	....
*Morphine	$C_{17}H_{19}NO_3$	10.30	4.50	Meconidine	$C_{21}H_{23}NO_4$	....	....
Pseudomorphine	$C_{17}H_{19}NO_4$	....	....	Cryptopine.....	$C_{21}H_{23}NO_5$	....	....
Hydrocotarnine.	$C_{12}H_{15}NO_3$	....	....	Laudanosine ...	$C_{21}H_{27}NO_4$	....	....
*Codeine	$C_{18}H_{21}NO_3$	0.25	1.52	*Narcotine	$C_{22}H_{23}NO_7$	1.30	3.47
*Thebaine	$C_{19}H_{21}NO_3$	0.15	....	Lanthopine	$C_{23}H_{25}NO_4$	....	....
Protopine.....	$C_{20}H_{19}NO_5$	....	....	*Narceine.....	$C_{23}H_{29}NO_9$	0.71	0.42
Rhœadine.....	$C_{20}H_{21}NO_6$	....	....	Porphyroxine ..	.....	....	....
Codamine.....	$C_{20}H_{25}NO_4$	....	...				

Morphine, $C_{17}H_{19}NO_3 + Aq.$—This alkaloid was probably obtained in an impure form by Boyle in the seventeenth century. In 1803 Seguin, Derosne, and Sertuerner almost simultaneously obtained crystalline principles from opium, but failed to recognize their basic character; it was only in 1817 that Sertuerner recognized the true nature of morphine, and was thus the first to discover a vegetable alkaloid.

Morphine crystallizes in colorless prisms; odorless, but very bitter; it fuses at 120°, losing its water of crystallization; more strongly heated, it swells up, becomes carbonized, and finally burns. It is soluble in 1000 pts. of cold water, in 100 pts. of boiling water; in 20 pts. of alcohol of 0.82, and in 13 pts. of boiling alcohol of the same strength; in 390 pts. of cold amyl alcohol, much more soluble in the same liquid warm; almost insoluble in aqueous ether; rather more soluble in alcoholic ether; almost insoluble in benzene; soluble in 60 pts. of chloroform. All the solvents dissolve morphine more readily and more copiously when it is freshly precipitated from solutions of its salts than when it has assumed the crystalline form.

Morphine combines with acids to form crystallizable salts, of which the chloride, sulphate, and acetate are used in medicine. The action of hydrochloric acid upon morphine is interesting; if morphine be heated for some hours with excess of hydrochloric acid, under pressure, to 150°, it loses water and is converted into a new base—*apomorphine*, $C_{17}H_{17}NO_2$—a valuble emetic, which may be administered hypodermically. It is a crystalline solid, soluble in ether.

Tests for morphine.—1st. Nitric acid colors it red, changing to yellow. 2d. If a fragment of morphine be moistened with cold concentrated sulphuric acid and allowed to stand twenty-four hours, a colorless solution remains, which turns pink or red on the addition of a trace of nitric acid. If, as is almost invariably the case, the sulphuric acid contain nitric acid, the red color is produced without addition of nitric acid. The fluid, when warmed, cooled, and diluted with water, turns deep mahogany brown on the addition of a splinter of potassium dichromate. 3d. A mixture of morphine and cane-sugar (one to four) added to concentrated sulphuric acid, communicates to it a dark red color, which, when dealing with very small quantities of morphine, can be brought out by the addition of a drop

of bromine water. 4th. Morphine reduces solutions of iodic acid with liberation of iodine. The test is best applied by adding to the morphine residue, on a watch-glass, a drop or two of chloroform, then a few drops of a solution of iodic acid, and stirring; if morphine be present, the chloroform is colored violet. This reaction is quite delicate, and, *in the absence of other reducing agents*, characteristic of morphine, as it is not brought about by any other vegetable alkaloid. 5th. A neutral solution of a morphine salt colors *neutral* solution of ferric chloride a deep blue. 6th. If a solution of molybdic acid in sulphuric acid (Fröhde's reagent) be added to a trace of morphine or of a morphine salt, it is colored a beautiful violet by the reduction of the molybdenum compound; the color gradually changes to blue, then to a dirty green, and finally to a very faint pink; it is instantly discharged on the addition of water. 7th. A solution of acetate of morphine, warmed with an ammoniacal solution of silver nitrate, produces a gray precipitate of metallic silver; the filtrate turns red or pink on the addition of nitric acid. 8th. Auric chloride forms, with solutions of morphine, a yellow precipitate, which subsequently turns violet-blue.

Codeine, $C_{18}H_{21}NO_3 + Aq.$—crystallizes in large rhombic prisms, or, from ether without water of crystallization, in octahedra; it is bitter; soluble in 80 pts. of cold water, 17 pts. of boiling water; very soluble in alcohol, ether, chloroform, benzene; almost insoluble in petroleum ether; fuses at 158°.

It dissolves in cold, concentrated sulphuric acid, the solution being colorless, but assuming a blue color after several days, or immediately on being warmed. Fröhde's reagent (see Morphine) dissolves it with a dirty green color, which, after a time, turns to blue. Neutral solution of ferric chloride is only colored blue by it after the addition of sulphuric acid. It combines with iodine to form a ruby-red or violet compound.

Codeine is probably derived from morphine by the substitution of methyl (CH_3) for an atom of hydrogen, $C_{17}H_{18}(CH_3)NO_3 = C_{18}H_{21}NO_3$, because, by acting upon codeine with hydrochloric acid, as in the formation of apomorphine from morphine, that base is formed along with methyl chloride:

$$\underset{\text{Codeine.}}{C_{18}H_{21}NO_3} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Apomorphine.}}{C_{17}H_{17}NO_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Methyl chloride.}}{CH_3Cl}$$

Narceine, $C_{23}H_{29}NO_9 + 2\ Aq.$—crystallizes in fine, prismatic needles; bitter; sparingly soluble in water, alcohol, and amyl alcohol—much more soluble in the same solvents when warm; insoluble in ether, benzene, and petroleum ether; it fuses at 92°; at 100° it loses 1 Aq., and the other at 140°; at which temperature it is decomposed into amorphous products.

It dissolves in concentrated sulphuric acid with a gray-brown color, which, slowly at ordinary temperatures, rapidly when heated, changes to blood-red. Fröhde's reagent colors it first dark olive-green, which passes after a time, or, when heated, to red; if an incipient red color have been obtained by heating the mixture, it on cooling gradually turns blue, beginning at the edges. It is colored blue-violet by iodine solution, like starch. A solution of iodine in potassium iodide solution causes, in narceine solutions, an amorphous brown precipitate, which, after a time, becomes crystalline and lighter in color.

Narcotine, $C_{22}H_{23}NO_7$—crystallizes readily in transparent prisms; fuses at 177°, and, when fused, crystallizes at 130°, and at 220° it is decomposed, ammonia is given off, and *hemipinic acid*, $C_{10}H_{10}O_5$, remains;

it is almost insoluble in water, readily soluble in alcohol, ether, and benzene, insoluble in petroleum ether, and in water faintly acidulated with acetic acid; chloroform removes it from its hydrochloric acid solution when the two are shaken together.

Its salts are for the most part uncrystallizable, unstable, and readily soluble in water and alcohol. Concentrated sulphuric acid dissolves it, the solution being at first colorless, but turns yellow in a few moments, and finally, after a day or two, red. Its solution in dilute sulphuric acid if very gradually evaporated, turns first orange-red, and then, from the periphery toward the centre, bluish violet, and finally, when the acid begins to volatilize, reddish violet. A solution of narcotine in cold concentrated sulphuric acid is colored red by the introduction of a trace of nitric acid; if the sulphuric acid contain nitric acid, the red color appears on dissolving the alkaloid. Fröhde's reagent dissolves it with a greenish color, passing to cherry-red.

Thebaine—*Paramorphine*—$C_{19}H_{21}NO_3$—probably the most actively poisonous of the opium alkaloids, crystallizes in white, silvery plates; fuses at 93°; is without taste when pure; insoluble in water, soluble in alcohol, ether, and benzene; its salts are readily soluble in water and alcohol.

Concentrated sulphuric acid is immediately colored bright red by it, the solution gradually turning yellowish red. Chlorine, bromine, and nitric acid attack it energetically. Fröhde's reagent behaves with it like sulphuric acid. Sulphuric acid containing nitric acid is colored reddish orange by it. Its solution in chlorine water is colored dark reddish brown by ammonia.

Meconic acid, $C_7H_4O_7+3Aq$.—a tribasic acid existing in opium in combination with a part, at least, of the alkaloids. It is obtained from the calcic meconate resulting from the preparation of morphine. It crystallizes in small prismatic needles; has an acid, astringent taste; loses its water of crystallization at 120°; quite soluble in water, soluble in alcohol, sparingly soluble in ether.

The characteristic reaction of meconic acid is the production of a blood-red color with ferric chloride; the color is not discharged by dilute acids or by mercuric chloride, but is discharged by stannous chloride and by alkaline hypochlorites (see p. 341).

The reactions of meconic acid and of narcotine are of great value to the toxicologist in enabling him to distinguish between poisoning by morphine and that by opium or its preparations.

Cinchona Alkaloids.

Although by no means so complex as opium, cinchona bark contains a great number of substances: quinine, cinchonine, quinidine, cinchonidine, aricine; quinic, quinotannic, and quinovic acids; cinchona red, etc. Of these the most important are quinine and cinchonine.

Quinine, $C_{20}H_{24}N_2O_2+_nAq$.—discovered in 1820, by Pelletier and Caventou. It exists in the bark of a variety of trees of the genera *Cinchona* and *China*, indigenous in the mountainous regions of the north of South America, which vary considerably in their richness in this alkaloid, and consequently in value; the best samples of calisaya bark contain from 30 to 32 parts per 1,000 of the sulphate; the poorer grades 4 to 20

parts per 1, 000; inferior grades of bark contain from mere traces to 6 parts per 1,000.

It is known in three different states of hydration, with one, two, and three molecules of water, and anhydrous. The anhydrous form is an amorphous, resinous substance, obtained by evaporation of solutions in anhydrous alcohol or ether. The first hydrate is obtained in crystals by exposing to air recently precipitated and well-washed quinine; the second by precipitating by ammonia a solution of quinine sulphate, in which hydrogen has been previously liberated by the action of zinc upon sulphuric acid; it is a greenish, resinous body, which loses H_2O at 150°. The third, that to which the following remarks apply, is formed in the processes of manufacture by precipitating solutions of quinine salts with ammonia.

It crystallizes in hexagonal prisms; is very bitter; fuses at 120°; becomes colored, swells up, and, finally, burns with a smoky flame. It does not sublime. It dissolves in 2,200 pts. of cold water, in 760 of hot water; very soluble in alcohol and chloroform; soluble in amyl alcohol, benzene, fatty and essential oils, and ether. Its alcoholic solution is powerfully lævogyrous, according to the most recent observations the value of $[a]_D = -270.7°$ at 18°, which is diminished by increase of temperature, but increased by the presence of acids.

The decompositions of quinine, although of great interest to the chemist as affording indications, slight at present, which may lead to its artificial production, are of little direct interest in this place.

Dilute sulphuric acid dissolves quinine, forming colorless, but fluorescent solutions (see below). Quinine, or its salts, in solution, is colored green when treated first with chlorine, and then with ammonia. A current of chlorine passed through water holding quinine in suspension, forms a red solution. A solution of quinine treated with chlorine water, and then with some fragments of potassium ferrocyanide, is colored pink, passing to red.

Quinine is not used in medicine in the free state, but in the form of its salts, the most important of which are:

Sulphate—Disulphate—Quiniæ sulphas—(U. S., Br.)—SO_4 $(C_{20}H_{24}N_2O_2)_2$ + 7 Aq.—is the form usually met with. It crystallizes in prismatic needles; very light; intensely bitter; phosphorescent when heated to 100°; fuses readily, loses its water of crystallization at 120°, turns red, and finally carbonizes; it effloresces on contact with air, losing 6 Aq.; soluble in 740 pts. of water at 13°, and in 30 pts. of boiling water; in 60 pts. of alcohol; almost insoluble in ether.

Its solution, mixed with an alcoholic solution of iodine, deposits a brilliant green crystalline compound. Quinine sulphate, in the presence of water, treated with an excess of dilute sulphuric acid, is dissolved, the solution containing the

Hydrosulphate, $SO_4H(C_{20}H_{24}N_2O_2)$ + 7 Aq.—which is consequently the salt present in most medicinal solutions of quinine. It may be crystallized in long, silky needles, or in short, rectangular prisms. It differs from the preceding salt in its much greater solubility in water, being dissolved by 11 pts. of that solvent at 13°. Its solutions exhibit in a marked manner the phenomena of fluorescence, being colorless, but showing a fine, pale blue color when illuminated by a bright light against a dark background, or by transmitted light.

Bisulphate, $C_{20}H_{24}N_2O_2(SO_4H_2)_2$ + 7 Aq.—a compound obtained by evaporating a solution of the preceding salt in the presence of an excess

of moderately concentrated sulphuric acid. It forms white, prismatic needles; very soluble in water; is colored reddish brown by exposure to light; its solution is highly fluorescent.

Owing to the high price of the salts of quinine, they are largely adulterated. Pure quinine should respond to the following tests: when a gram of it is shaken up in a test-tube with 15 c.c. of ether and 2 c.c. of aqua ammoniæ, the liquids should subsequently separate into two clear layers, without any milky zone between them (cinchonine). When dissolved in hot water, precipitated with an alkaline oxalate and filtered, the filtrate should not precipitate with ammonia (quinidine). It should be completely soluble in water acidulated with sulphuric acid (fats, resins). It should dissolve completely in dilute, boiling alcohol (gum, starch, alkaline and earthy salts). It should not be blackened by sulphuric acid (cane-sugar). It should not be colored red or yellow by sulphuric acid (salicin and phlorizin). When burned upon platinum foil, it should leave no residue (mineral substances).

Cinchonine—$C_{20}H_{24}N_2O$—accompanies quinine in Peruvian bark, in which it is present in less amount, varying from 2 to 12 pts. per 1,000; and in some cases, as in yellow Guayaquil bark, reaching 30 pts. per 1,000.

It crystallizes in colorless prisms or needles without water of crystallization; fuses at 150°, and at 220° is partly sublimed in fine needles and partly decomposed; it is soluble in 3,810 pts. of water at 10°, in 2,500 pts. of boiling water; in 140 pts. of alcohol of sp. gr. 0.852 at 10°; in 371 pts. ether at 20°; in 40 pts. chloroform; dextrogyrous, $[a]=+190.4°$; alkaline; bitter.

Although cinchonine differs from quinine in composition only by one atom of oxygen less, all attempts to convert the former into the latter alkaloid by oxidation have only resulted in the formation of an isomere of quinine—*oxycinchonine*.

The salts of cinchonine resemble those of quinine in composition, but differ from them in being much more soluble in water and alcohol, and in not being fluorescent; they are permanent in air, and become phosphorescent when heated to 100°.

Two other alkaloids derived from plants related to the cinchona require mention.

Caffeine—*Theine*—*Guaranin*—$C_8H_{10}N_4O_2$ + Aq.—exists in coffee, tea-leaves, Paraguay tea, and other plants.

It crystallizes in long, silky needles; faintly bitter; soluble in 93 pts. of water at 12°, 158 pts. strong alcohol, or 218 pts. ether. Hot, fuming nitric acid converts it into a yellow liquid, which turns purple on the addition of ammonia; on boiling, the mixture is decolorized and white crystals of *cholestrophane*, a methyl derivative of parabanic acid (*q. v.*), separate. Chlorine acting on caffeine in the presence of water, yields a methyl derivative of alloxantine (*q. v.*)—*amalic acid*.

Emetine—$C_{30}H_{44}N_2O_5$—a poisonous alkaloid to which ipecacuanha owes its activity. It appears as a white, amorphous, somewhat bitter powder, almost insoluble in cold water; sparingly soluble in hot water, alcohol, chloroform, and ether; soluble in benzene and petroleum ether.

Concentrated sulphuric acid forms with it a greenish brown solution. Sulphuric acid containing nitric acid colors it green, changing to yellow. Fröhde's reagent dissolves it immediately with a red color, passing soon to a yellowish green, then to green.

Alkaloids of the Loganiaceæ.

Strychnine, $C_{21}H_{22}N_2O_2$—discovered in 1818 by Pelletier and Caventou, in the St. Ignatius bean and subsequently in other varieties of *Strychnos*. The sources from which the alkaloid is now almost exclusively obtained are the seeds of the *Strychnos nux vomica*, and the bark of the same tree, known as *false Angostura bark;* the seeds contain about 0.5 per cent of strychnine.

Strychnine crystallizes upon spontaneous evaporation of its solutions in orthorhombic prisms; by rapid evaporation or sudden cooling of its solutions it separates as a white powder. Its solutions are alkaline in reaction and have an intensely bitter taste, which is perceptible in a solution containing only 1 part in 600,000. It is very sparingly soluble in water (in 6,667 parts of cold and in 2,500 parts of warm water). Its solubility in alcohol varies with the strength of the solvent; it is insoluble in absolute alcohol; 1 part of strychnine is soluble in 120 parts of alcohol of sp. gr. 0.863 at the ordinary temperature, and in 10 parts of the same alcohol at the boiling-point; a weaker alcohol, of sp. gr. 0.936 dissolves 1 part in 240 in the cold. It is insoluble in absolute ether, very sparingly soluble in commercial ether. Benzene and amyl alcohol dissolve 1 part to 200–250. Its best solvent is chloroform, which is capable of dissolving twenty per cent. of strychnine. It is also sparingly soluble in creasote, the fatty and volatile oils, glycerin, and carbon disulphide. From most of these solutions it may be obtained in the crystalline form by evaporation. The alcoholic solutions are lævogyrous, $[a]j = -132°$—136°; the acid solutions are much less active. Strychnine cannot be fused without undergoing decomposition, and is only partially capable of sublimation.

Strychnine is a powerful base; it neutralizes the strongest acids, being dissolved (with formation of a sulphate) without decomposition in concentrated sulphuric acid; it also precipitates many metallic oxides from solutions of the corresponding salts.

The salts of strychnine are for the most part crystallizable, soluble in water and in alcohol, and are all intensely bitter. Of the salts of strychnine the *neutral sulphate*, $SO_4H_2(C_{21}H_{22}N_2O_2)_2+7Aq.$, is generally used medicinally in place of the alkaloid; it crystallizes in rectangular prisms, soluble in ten parts of water; the water of crystallization is driven off by heat or in vacuo. The *acetate* is exceedingly soluble in water, and only crystallizes in the presence of an excess of acid.

By the action of chlorine upon solutions of strychnine, compounds are obtained in which one or three atoms of hydrogen are replaced by atoms of chlorine; these chlorine derivatives possess basic properties. By the action of iodine upon strychnine, a peculiar substance called *iodostrychnine*, $4C_{21}H_{22}N_2O_2,3I_2$, is obtained, which crystallizes in alcoholic fluids in golden yellow scales.

The iodides of methyl and of ethyl react energetically with strychnine, to form the iodides of *methyl* or *ethylstrychnium*, which bear the same relation to the alkaloid that the iodide of ammonium bears to ammonia. These substances are white, crystalline solids, basic in their nature, which in common with similar derivatives of other alkaloids possess the power, when injected subcutaneously, of producing effects very similar to those of curarine (*q. v.*).

By the action of potassium nitrite upon a boiling aqueous solution of

strychnine sulphate, nitrogen is given off and two oxidized products are formed; one, which crystallizes in fine orange-yellow crystals, is *oxystrychnine*, $C_{21}H_{22}N_2O_6$; the other, forming red crystals, is *bioxystrychnine*, $C_{21}H_{22}N_2O_7$.

When strychnine is acted upon, with proper precautions, by sulphuric acid and potassium chlorate, a crystallizable acid called *strychnic acid* is formed; it seems to be the same substance which, under the name *igasuric acid*, has been obtained from St. Ignatius' beans, and with which the alkaloid is probably in combination in nature.

Tests for strychnine.—1st. It dissolves without decomposition in concentrated sulphuric acid, the solution being colorless if the alkaloid be pure. The alkaloid is precipitated when the solution is diluted and the acid is neutralized, preferably with magnesia in very slight excess. 2d. When a fragment of any substance, capable of yielding nascent oxygen on contact with concentrated sulphuric acid, is added to a solution of strychnine in that acid, the following colors appear: a very transitory blue (frequently not perceptible); a brilliant violet, which slowly changes to rose-pink, and this in turn to yellow. Of the various oxidizing agents which have been recommended, we believe potassium dichromate to be the best for the purposes of this test, notwithstanding the opposite opinion expressed by Letheby and echoed verbatim by Woodman and Tidy.

The test is best applied by evaporating, upon a procelain dish or a watch-glass (when the latter is used it must be placed upon a white surface when the dichromate is added), a drop or two of the solution suspected of containing strychnine; the residue is treated with one or two drops of concentrated sulphuric acid, which is spread out with a glass rod; a small fragment (not powder) of potassium dichromate is then placed upon a dry part of the watch-glass and pushed with moderate rapidity from one part of the moistened surface to another; if strychnine be present, the course of the dichromate will be marked by a violet streak, which passes through rose-pink to yellow.

This reaction is of great delicacy, being capable of showing the presence of $\frac{1}{50000}$ grain of strychnine, and if applied to a residue suitably obtained (see p. 348), is characteristic of the alkaloid. The only known substance, in fact, which produces the same play of colors under like conditions, is curarine; but, as this substance is quite soluble in water and does not pass from its alkaline aqueous solution into the solvents used in the process of separation, it cannot find its way into the solutions in which strychnine is sought for, and cannot, therefor, give rise to any error. A somewhat similar reaction is produced by aniline, which may, however, be readily distinguished from strychnine by its being liquid or oily, while strychnine is solid; by its peculiar odor, strychnine being odorless; and by the fact that the reaction only takes place with *dilute* sulphuric acid in the case of aniline, and with the concentrated acid in the case of strychnine. The presence of morphine also interferes to a certain extent with the action of this test, an interference which is, however, of but slight practical importance, as morphine is not found in the same residue as strychnine (p. 349). In the presence of brucine the reaction takes place more slowly, the color only appearing after oxidation of the brucine. 3d. A dilute solution of potassium dichromate produces in solutions of strychnine a yellow crystalline precipitate of strychnine chromate. Otto utilizes the formation of this salt for the production of the color reaction (2); he advises that the residue containing strychnine be moistened with dilute solution of potassium dichromate (1 in 200); after a

few moments the fluid is poured off, the deposit washed, and treated with concentrated sulphuric acid, when the characteristic play of colors is observed. 4th. If a solution of strychnine be evaporated in a depression in a strip of platinum foil, the residue moistened with concentrated sulphuric acid, the foil connected with the positive pole of a single cell of Grove's or Smee's battery, and a platinum wire from the negative pole brought in contact with the surface of the acid, a violet color appears upon the surface of the foil (Letheby). 5th. Solutions of strychnine and of its salts are intensely bitter, the taste being distinguishable in a solution containing one part of the alkaloid in six hundred thousand of water. 6th. If a solution of strychnine be introduced beneath the skin of the back of a frog, the animal exhibits the symptoms of strychnine-poisoning: difficulty of respiration; tetanic convulsions induced by the slightest irritation, as by striking the table or blowing upon the animal; twitching of the muscles during the intervals between the convulsions; dilatation of the pupils during the convulsions, and contraction during the intervals; usually emprosthotonos, sometimes opisthotonos. The smallest frogs should be selected, and they should be dried with bibulous paper before the injection of the solution. This test, which was first suggested by Marshall Hall, is very delicate; $\frac{1}{18000}$ grain of the acetate ($=\frac{1}{18000}$ strychnine) injected into a small frog have produced tetanic spasms in nine and one-half minutes, and death in two hours. 7th. When solid strychnine, or a residue containing it, is moistened with a solution of iodic acid in sulphuric acid a yellow color appears, which soon changes to brick-red, and finally to a violet-red (Selmi). 8th. Moderately concentrated nitric acid, in the cold, colors strychnine yellow; a pink or red color indicates the presence of brucine.

Strychnine is one of the most stable of the alkaloids, and may remain for a long time in contact with putrefying animal matter without undergoing decomposition.

Antidotes.—Chloroform, emetics, the stomach-pump, chloral hydrate.

Brucine, $C_{23}H_{26}N_2O_4$—discovered in 1819 by Pelletier and Caventou, is obtained from the alcoholic washings in the preparation of strychnine. It forms transparent, oblique, rhomboidal prisms, containing four molecules of water of crystallization, which are readily given off by exposure to dry air. It fuses a little above 100°, and, on cooling, forms an amorphous, waxy mass. Effloresced brucine dissolves in 500 pts. of boiling, and in 850 pts. of cold water; the newly crystallized alkaloid is more soluble; it is easily soluble in alcohol, chloroform, and amylic alcohol; less soluble in benzene, benzine, glycerin, and the volatile oils; insoluble in ether and in the fatty oils. It is odorless, intensely and persistently bitter.

Brucine is a powerful base, forming salts which are, for the most part, crystallizable and soluble in water. It forms compounds similar to methyl-, ethyl-, and iodo-strychnine under like conditions. Its action upon the animal economy is similar to that of strychnine, but much less energetic.

Tests for brucine.—1st. Concentrated nitric acid gives with brucine a bright scarlet color, which soon assumes a yellowish tinge, and finally becomes yellow, especially if heated; upon the addition of stannous chloride or of colorless ammonium sulphydrate to the red fluid, it is turned to an intense violet. 2d. A solution of brucine assumes a bright red color upon the addition of chlorine water or of chlorine gas, the color changing to yellowish brown upon the addition of ammonium hydrate.

The separation of brucine from strychnine is best effected by adding

to a solution of the mixed acetates, not too dilute, a solution of potassium dichromate; the strychnine is precipitated as the chromate, while the brucine remains in the solution.

Igasurine—an alkaloid discovered in nux vomica by Desnoix. In poisonous activity it is intermediate between strychnine and brucine, which alkaloids it resembles in the nature of its action upon the economy.

Curarine, $C_{10}H_{14}N$—an alkaloid obtained from *curare* or *worara*, a South American arrow-poison. It crystallizes in four-sided, hygroscopic prisms; very bitter; faintly alkaline; very soluble in water and in alcohol; insoluble in ether and benzene.

Concentrated sulphuric acid colors it blue; upon the addition of a crystal of potassium dichromate to this solution, the same changes of color as with strychnine (*q. v.*) are observed, but they take place more slowly. Nitric acid colors it purple.

Alkaloids of the Solanaceæ.

The alkaloids of this class are solanine, dulcamarine, atropine, belladonine, hyoscyamine, lycine, and duboisine.

Solanine, $C_{43}H_{69}NO_{16}$—obtained from many species of *Solanum*. It crystallizes in small, white, shining prisms; faintly bitter and nauseous in taste; sparingly soluble in water, alcohol, and ether.

Concentrated sulphuric acid colors it orange-red, passing to violet and then to brown. Nitric acid colors it yellow.

Atropine—*Daturine*—$C_{17}H_{23}NO_3$—is the active principle of *belladonna*. It crystallizes in colorless needles; strongly and persistently bitter; alkaline; sparingly soluble in water, benzene, and ether; very soluble in chloroform; it volatilizes when its solutions and those of its salts are boiled. If a fragment of potassium dichromate be dissolved in a few drops of concentrated sulphuric acid, the mixture warmed, a fragment of atropine, and then a drop or two of water added, the mixture being stirred, an odor resembling that of orange-blossoms is observed.

Hyoscyamine, $C_{18}H_{17}NO$ (?)—the active principle of *hyoscyamus niger*. It forms a yellowish mass, drying with difficulty; has an odor of tobacco, and a sharp, disagreeable taste; rather soluble in water, easily soluble in alcohol, ether, chloroform, and benzene.

Duboisine is a newly discovered alkaloid, obtained from a New Caledonian plant, whose characters appear to resemble those of atropine.

Alkaloids from Other Sources.

Colchicine, $C_{17}H_{19}NO_5$—from *Colchicum autumnale*. Sulphuric acid colors it yellow, then green. Nitric acid colors it violet, then green. Sulphuric acid, containing nitric acid, colors it violet, turning to orange on the addition of an alkali.

Veratrine, $C_{32}H_{49}N_2O_8$—from *Veratrum album* and *V. viride*. Cold sulphuric acid colors it first yellow, then red, and finally purple. Bromine water colors it violet, violet-red. Pure boiling hydrochloric acid colors it red.

Muscarine—from *Agaricus muscarius*.

Physostigmine—*Eserine*—$C_{15}H_{21}N_3O_2$—from *Physostigma venenosum*, Calabar bean. Sulphuric acid colors it yellow, passing, after a time,

to red, or to reddish brown, on the addition of bromine water. Hypochlorites color it red at first; the color is discharged by an excess of the reagent.

Cocaine, $C_{17}H_{21}NO_4$—from *Erythroxylon coca.*

Aconitine, $C_{30}H_{47}NO_7$—from *Aconitum napellus.* When dissolved in aqueous phosphoric acid, and the solution carefully evaporated over a small flame, it produces a violet color at a certain point of concentration. Dissolved in concentrated sulphuric acid at ordinary temperatures, the solution is at first yellow, and passes very slowly through brown and red-brown to violet.

Pilocarpine—the recently discovered alkaloid of *jaborandi.* It is a crystalline base, forming crystallizable salts.

Ptoamines—*Septicine.*—Under these names substances of great interest to the toxicologist have been described in the past few years; they are alkaloids obtained from animal tissues in complete or incipient putrefaction. They react with the general reagents for the alkaloids; some are fixed, others volatile; some are soluble in ether, others insoluble in ether, but soluble in amyl acohol; others insoluble in both liquids; some are strong reducing agents and respond to the iodic acid test for morphine. They give the following color reactions, which may appear or be absent according to the extent to which the putrefaction has progressed, and to the method of extraction: with moderately concentrated sulphuric acid a violet-red; the same color with hydrochloric acid containing sulphuric acid and warmed; with sulphuric acid and bromine water a more or less distinct red, which gradually fades; warmed with nitric acid and afterward treated with potassium hydrate, a golden-yellow; with iodic acid, sulphuric acid, and sodium bicarbonate, a more or less distinct violet-red. They are readily oxidizable, turn brown on contact with air, and give off odors resembling those of urine in some instances, of coniine in others, and of certain flowers in others. They are pungent in taste, and produce a sense of numbness in the tongue, and a tickling sensation in the throat. Of those soluble in ether or in amyl alcohol, some are non-poisonous, and others actively toxic.

Although these substances present such striking analogies with the vegetable alkaloids, they differ from the more usually employed of the vegetable poisons sufficiently, and in one or more prominent character to such an extent, that any fear of their being mistaken for a vegetable poison by the toxicologist is groundless.

ALBUMINOIDS.

Protein Bodies.

The substances of this class, exceedingly complex in their chemical composition, are the *organic substances,* par excellence, being never absent in living vegetable or animal cells, to whose "life" they are indispensable.

They are composed of carbon, hydrogen, oxygen, nitrogen, and sulphur; for the most part uncrystallizable, and prone to putrefaction. They are, with some notable exceptions (see Peptones), colloids, and, as such, incapable of dialysis. They are all, when dissolved, lævogyrous, and for the most part soluble in water.

Although the individual members of the group differ from each other

considerably in their characters, they have many properties in common. Thus, they respond to the following *General Tests:* 1st. *Millons' reagent* is made by dissolving, by the aid of heat, one part of mercury in two parts of nitric acid, sp. gr. 1.42; after solution of the mercury, the liquid is diluted with twice its volume of water, and, after standing twenty-four hours, decanted from the deposit. This reagent, added to a solution containing a trace of an albuminoid, colors it purple-red when warmed to about 70°. 2d, *Xanthoproteic reaction.*—Nitric acid colors the albuminoids yellow, the color changing to orange on the addition of ammonia. 3d. *Pettenkofer's reaction* is produced by the albuminoids (see p. 212). 4th. If a solid albuminoid be touched with a drop of cupric sulphate solution, and then with a drop of caustic potassa solution, and finally washed, a violet mark remains. The same effect is produced in solutions (see p. 264). 5th. A solution of an albuminoid in excess of glacial acetic acid is colored violet, and rendered faintly fluorescent, when treated with concentrated sulphuric acid. 6th. Solutions of the albuminoids strongly acidified with acetic acid give a white precipitate with potassium ferrocyanide.

Decompositions.—When heated with dilute acids they are decomposed into two substances: one insoluble, amorphous, yellowish, called *hemiprotein;* the other, soluble in water, insoluble in alcohol, faintly acid, called *hemialbumin.* A prolonged boiling with moderately concentrated sulphuric acid decomposes the albuminoids into well-defined bodies—leucin, tyrosin; aspartic, and glutamic acids.

Alkalies dissolve the albuminoids more or less readily, forming soluble compounds (see below); when the solution is boiled, a part of the sulphur separates in the form of sulphide and hyposulphite. From the alkaline solution a substance is precipitated by acids, which is Mulder's *protein,* identical with albumin. Concentrated alkaline solutions decompose them into amido-acids. By fusion with alkalies, alkaline cyanides are also produced. The action of caustic baryta upon albuminoids has been productive of most interesting results in the hands of Schützenberger. When heated with caustic baryta and water to 100°, carbonate, sulphate, oxalate and phosphate of barium are deposited, and carbon dioxide and ammonia given off in the same proportions as would result if urea were similarly treated; upon raising the temperature, and finally heating, under pressure, at 200°, a crystalline mass is obtained which contains oxalic and acetic acids, a number of amido-acids, aspartic and glutamic acids, and a substance resembling dextrin.

Heated with water, under pressure, at 100°, they are partly dissolved and partly decomposed. When exposed to air and moisture they *putrefy,* with formation of ammonia, ammonium sulphydrate, carbon dioxide, volatile fatty acids, amido-acids of the fatty series, lactic acid, indol (?), alkaloids.

The products of the action of oxidizing agents upon the albuminoids vary with the agent used. A mixture of sulphuric acid and manganese dioxide or potassium dichromate, produces aldehydes and acids of the fatty and benzoic series, hydrocyanic acid and cyanides. Nitric acid forms xanthoproteic acid (see above), and, afterward, derived acids of the benzoic series. Bromine and water heated, under pressure, with albuminoids, yield carbon dioxide, oxalic and aspartic acids, amido-acids, and bromine derivatives of the fatty and benzoic series. Potassium permanganate produces from the albuminoids urea, carbon dioxide, ammonia, and water.

Constitution.—Although our knowledge of the constitution of these complex bodies is still very imperfect, the researches of Schützenberger

and others render it probable that they are complex amides, related to the ureids (*q. v.*), and formed by the combination of glycollamine, leucine, tyrosine, etc., with oxygenated radicals of the acetic and benzoic series.

Classification.—In the present state of our knowledge, the only classification of these substances which can be adopted is a temporary one, based more upon the physiological relations of the albuminoids than upon their chemical characters.

I.—*Soluble in pure water, coagulated by heat.*—The members of this class are the true *albumins* of the white of egg, serum, and vegetable albumin.

II.—*Insoluble in pure water, soluble in water without alteration in the presence of neutral salts, alkalies, and acids, and capable of precipitation unchanged from these solutions.*

1. *Globulins.*—Vitellin, myosin, paraglobulin, fibrinogen.
2. *Animal caseins.*—Milk casein, serum casein.
3. *Vegetable caseins.*—Gluten casein, legumin, conglutin.
4. *First terms of decomposition of the albuminoids by acids, alkalies, and soluble ferments.*—Albuminates (so-called), acid albumin, syntonin, hemiprotein, peptones.

III.—*Insoluble in water and only soluble after decomposition. Cannot be separated without alteration from their solutions in acids and alkalies.*—Glutin-fibrin, gliadin, mucedin.

IV.—*Coagulated by heat.*—Coagulated albumin and fibrin.

V.—*Amyloid matter.*—Lardacein.

VI.—*Collagene bodies.*—Collagen, elastin, ossein and its derivatives, chondrigen, chondrin, gelatin, keratin.

VII.—*Mucilaginous bodies.*—Mucin, paralbumin, colloidin.

I.—**Egg albumin** is the longest known of the albuminoids and exists in solution, imprisoned in a network of delicate membranes, in the white of egg. It is readily obtained in an impure condition by cutting the whites of eggs with scissors, expressing through linen, diluting with an equal volume of water, filtering and concentrating the filtrate at a temperature below +40°; mineral salts, which adhere to it tenaciously, are separated by dialysis. It seems to be a mixture of two different substances, one of which coagulates at 63°, and has the rotary power $[\alpha]j = -43°$; the other coagulates at 74°, and has the value of $[\alpha]j = -26°$.

Its solutions are not precipitated by a small quantity of hydrochloric acid, but an excess of that acid produces a deposit which is difficultly soluble in hydrochloric acid, water, and salt solution. Its characteristic reaction is that it is coagulated by agitation with ether.

Serum-albumin exists in blood-serum, chyle, lymph, pericardial fluid, the fluids of cysts and of transudations, in milk and, pathologically, in the urine. It is best obtained from blood-serum, after removal of paraglobulin (*q. v.*), by a tedious process, and only then in a state of doubtful purity. It is less abundant in the blood of some animals than paraglobulin, but more abundant in that of man.

Solutions of serum-albumin are lævogyrous $[\alpha]j = -56°$; they are not precipitated by carbon dioxide, by acetic or orthophosphoric acid, by ether or by magnesium sulphate. They are precipitated by mineral acids, tannic acid, metaphosphoric acid, and most metallic salts. When heated they become opalescent at 60°, and coagulate in the flocculent form at 72°—75°.

Detection and determination of albumin in urine.—The detection of albumen in the urine can be effected by the test by heat, combined with

that by nitric acid. The clear filtered urine, if alkaline, is *just* acidulated with acetic acid and then heated to boiling; if albumin be present, a cloudiness, or precipitate, or even complete solidification, will ensue, and will not disappear, but rather augment, on the addition of concentrated nitric acid. Neither test alone affords conclusive evidence of the presence of albumin. That by heat, while it coagulates albumin, also precipitates earthy phosphates if they be present in excess; but these are dissolved on the addition of nitric acid. Nitric acid, although it coagulates albumin and dissolves the phosphates, precipitates urates if present in excess, but, on the other hand, the urates are more soluble in hot than in cold solutions, and, consequently, are not precipitated by heat.

The acidulation of the alkaline urine, previous to heating, is imperative, as such urine does not respond to the heat-test if it contain a small quantity of albumin, unless it be acidulated; nitric acid should not be used for this purpose, nor should more acetic acid be added than just suffices to render the reaction acid.

The only chemical method, hitherto devised, of determining the quantity of albumin in urine with an approach to accuracy, is gravimetric. Twenty to fifty cubic centimetres of the filtered urine, according as the qualitative testing shows albumin to be present in large or small quantity, and diluted with water if the amount of albumin has been sufficient to cause solidification, are slowly heated over the water-bath, and, as the boiling temperature is approached, three to four drops of acetic acid are added; after the urine has been at 100° for a few moments, it is thrown upon a filter. The coagulum is washed with boiling water, then with water acidulated with nitric acid, then with alcohol, and finally, with ether; these repeated washings not only remove impurities, but cause the coagulum to contract, so that it can be readily detached and transferred to a weighed watch-glass; upon this it is dried at 115° and the whole weighed.

The determination of albumen by the polarimeter or by volumetric methods does not afford satisfactory results.

Vegetable albumin exists in solution in all vegetable juices, and forms the most valuable constituent of those vegetables which are used as food. It is coagulated from its solutions at 61°—63°, and by nearly all acids.

II.—**Vitelin** exists in the yolk of egg and in the crystalline lens. It is soluble in dilute solution of sodium chloride, from which it is precipitated by excess of water, by heating to 75°—80°, and by alcohol. It is not precipitated by solid sodium chloride. It dissolves in weak alkaline solutions without alteration and in very dilute hydrochloric acid (one to one thousand), by which it is quickly converted into syntonin.

Myosin is one of the principal constituents of the muscular fibre in rigor mortis. As obtained by Kühne it is a faintly yellow, opalescent, distinctly alkaline liquid, which, when dropped into distilled water, deposits the myosin in globular masses, while the water assumes an acid reaction. It is insoluble in water, easily soluble in dilute salt solution, from which it is precipitated by the addition of solid sodium chloride, or by a heat of 55°—60°. Very dilute hydrochloric acid dissolves and converts it into syntonin.

Paraglobulin.—This substance has been described by various authors under the names: *plasmine* (Denis), *serum casein* (Panum), *serum globuline, fibrino-plastic matter* (Schmidt), *serin* (Denis), and has been the subject of a vast amount of research.

It exists in blood-serum, in pericardial fluid, hydrocele fluid, lymph

and chyle, from which it is obtained by diluting with ten to fifteen volumes of ice-cold water, treatment of the solution with a strong current of carbon dioxide, and washing the collected deposit with water as long as a portion of the filtrate precipitates with acetic acid and potassium ferrocyanide, or with silver nitrate. As so obtained it is a granular substance, which gradually becomes more compact; insoluble in water, sparingly soluble in water containing carbon dioxide; soluble in dilute alkalies, in lime-water, in solutions of neutral alkaline salts, in dilute acids. Its solution in very dilute alkaline fluids is perfectly neutral and is not coagulated by heat, except after *faint* acidulation with acetic or mineral acids; it is precipitated by a large volume of alcohol; its solutions are also precipitated incompletely by dissolving sodium chloride in them to saturation, and completely by similar solution of magnesium sulphate; this last method of precipitation is used for the separation of paraglobulin from serum-albumin (see Fibrin).

Fibrinogen; after the separation of paraglobulin from blood-plasma, as described above, if the liquid be still further diluted and again treated with carbon dioxide, a substance is obtained which, although closely resembling paraglobulin in many characters, is distinct from it, and, unlike paraglobulin, it cannot be obtained from the serum separated from coagulated blood.

Paraglobulin and fibrinogen are both soluble in a solution of sodium chloride containing five to eight per cent. of the salt; when the degree of concentration of the salt solution is raised to twelve to sixteen per cent., the fibrinogen is precipitated, while the paraglobulin remains in solution and is only precipitated, and then incompletely, when the percentage of salt surpasses twenty (see Fibrin).

Milk casein, the most abundant of the albuminoids of the milk of mammalians, closely resembles alkali albuminates, with which it is probably identical, as the main point of distinction has been found to be without significance; unlike pure alkali albuminates, casein is coagulated from its solution by rennet (the product of the fourth stomach of the calf) at 40°; but it has been found that alkali albuminate is also so coagulated when milk-sugar and fat are added to the solution.

Milk.—The secretion of the mammary gland is water holding in solution casein, albumin, lactose, and salts, and fat in suspension. *Cream* consists of the greater part of the fat, with a small proportion of the other constituents of the milk. *Skim milk* is milk from which the cream has been removed. *Buttermilk* is cream from which the greater part of the fat has been removed, and consequently is of about the same composition as skim milk.

The composition of milk differs in animals of different species:

	Human.	Cow.	Goat.	Sheep.	Ass.	Mare.	Cream.	Condensed milk.
Water....	88.35	84.28	86.85	83.30	89.01	90.45	45.99	25.68
Solids	11.65	15.72	13.52	16.60	10.99	9.55	54.01	74.32
Casein ...	3.15	3.57	2.53	5.73	3.57	2.53	6.33	16.83
Albumin..		0.78	1.26					
Fat	3.87	6.47	4.34	6.05	1.85	1.31	43.97	10.27
Lactose...	4.37	4.34	3.78	3.96	5.05	5.43	3.28	44.33*
Salts	0.26	0.63	0.65	0.68		0.29	0.42	2 80

* Including 28.98 parts of cane-sugar.

The composition of cows' milk varies considerably according to the age, condition, breed and food of the cow; to the time and frequency of milking; and to whether the sample examined is from the first, middle, or last part of each milking.

Cows' milk is very frequently adulterated, both by the removal of the cream and the addition of water. For ordinary purposes, the purity of the milk may be determined by observing the specific gravity and the percentage of cream by the lactometer and creamometer, *neither of which, used alone, affords indications which can be relied upon.* The specific gravity should be observed at the temperature for which the instrument is made, as in a complex fluid such as milk no valid correction for temperature is practical; it ranges in pure milk from 1027 to 1034, it being generally the lower in milk which has been watered, and in such as is very rich in cream, and the higher the less cream is present. The following table, from Hassall, indicates the relations between specific gravity and percentage of cream:

Specific gravity at 15.5° ..	1034.5	1029.7	1030.4	1031.3	1032.1	1027.5
Cream by creamometer...	9.0	7.5	11.0	9.0	11.0	20.5
Specific gravity at 15.5° ..	1031.2	1028.8	1030.3	1032.3	1029.9	1030.6
Cream by creamometer...	21.0	12.0	15.3	18.3	13.2	13.8

Average specific gravity, 1030.7. Average per cent. of cream, 13.5.

The percentage of cream is determined by the creamometer: a glass tube about a foot long and half an inch in diameter, the upper fifth (excluding about an inch from the top) being graduated into hundredths of the whole, the 0 being at the top. To use it, it is simply filled to the 0 with the milk to be tested, set aside for twenty hours and the point of separation between milk and cream read off. It should be above eight per cent.

This method of determining the purity of milk, although sufficient for ordinary purposes, should not be considered as affording evidence upon which to base legal proceedings; in such cases nothing short of a chemical determination of the percentage of fat, and of solids not fat. should be accepted as evidence of the impurity of milk.

Serum-casein is a substance obtained by Kühne and Eichwald from blood-serum diluted with ten volumes of water, freed from paraglobulin by carbon dioxide, and from albumin by acetic acid and heat. It is insoluble in salt solutions, slowly soluble in a one per cent. solution of sodium hydrate. Such a solution is partially precipitated by carbon dioxide, almost completely by acetic acid, and completely by heating with excess of powdered sodium chloride; incompletely soluble in dilute hydrochloric acid.

Gluten-casein.—That portion of crude gluten (a soft, elastic, grayish material best obtained from flour) which is insoluble in alcohol, hot or cold; **Legumin,** a sparingly soluble albuminoid obtained from peas, beans, etc.; and **Conglutin,** a substance closely related to legumin and to *gliadin,* but differing from them in some characters, obtained from almonds, are three vegetable albuminoids resembling casein.

They are insoluble in pure water, readily soluble in dilute alkaline solutions, from which they are precipitated by acids and by rennet.

Alkali albuminates—*proteins* of Hoppe Seyler—are formed when an

albuminoid is dissolved in concentrated solutions of potassium and sodium hydrates; it is very probable that they are identical with serum and milk-casein.

Acid albumins are substances obtained by precipitating solutions of albuminoids by the simultaneous addition of an acid and a large quantity of a neutral salt; they vary exceedingly in composition and properties.

Syntonin, *parapeptone,* is extracted from contractile tissues; the same substance is formed by the action of dilute acids upon the albuminoids, and as the first product of the action of the gastric juice, or of mixtures of pepsin and dilute sulphuric acid upon albuminoids. It resembles serum casein closely, the only divergence in their properties being that syntonin is much more readily soluble in a 0.1 per cent. solution of hydrochloric acid, and in faintly alkaline liquids.

Peptones, *albuminose,* are the products of the action of the gastric and pancreatic juices upon albuminoids during the process of digestion.

They are soluble in water, insoluble in alcohol and ether. Their watery solutions are neutral, are not precipitated by acids or alkalies, or by heat when the liquid is faintly acid. Alcohol precipitates them in white, casein-like flocks, which, if slowly heated to 90° while still moist, form a transparent, yellowish liquid, and, on cooling of the liquid, an opaque, yellowish, glassy mass.

The most important character of the peptones is that they differ from other albuminoids in being capable of dialysis through animal membranes. Their presence in the blood has not been demonstrated, even in the portal vein; it is therefor probable that, almost immediately after their entrance into the circulation, they are reconverted into albuminoids resembling, although differing from, those from which they were derived.

IV.—**Coagulated albumins** are obtained, as described above, from the soluble varieties by the action of acids, heat, alcohol, etc. They are insoluble in water, alcohol, solutions of neutral salts, dilute hydrochloric acid; difficultly soluble in dilute alkaline solutions. In acetic acid they swell up and dissolve slowly; from this solution they are precipitated by concentrated salt solution. Concentrated hydrochloric acid dissolves them with formation of syntonin. By the action of gastric juice, natural or artificial, they are converted first into syntonin, then into peptones.

Fibrin is obtained when blood is allowed to coagulate or is whipped with a bundle of twigs. When pure it is at first a gelatinous mass, which contracts to a white, stringy, tenacious material, made up of numerous minute fibrils; when dried it is hard, brittle, and hygroscopic. It is insoluble in water, alcohol, ether; in dilute acid it swells up and dissolves slowly and incompletely. When heated with water to +72°, or by contact with alcohol, it is contracted, and is no longer soluble in dilute acids, but soluble in dilute alkalies. In solutions of many neutral salts of six to ten per cent., it swells up and is partially dissolved; from this solution it separates on the addition of water, or upon the application of heat to +73°, or by acetic acid or alcohol. Moist fibrin has the curious property of decomposing oxygenated water with copious evolution of oxygen.

Fibrin does not exist as such in the blood, and the method of its formation and of the clotting of blood has been the subject of a vast amount of experiment and argument; nor can the question be said to be definitely set at rest. In the light of the researches of Denis, Schmidt, and especially of Hammarsten, it may be considered as almost proven that fibrin is formed from fibrinogen under favorable circumstances, and by a transfor-

mation which is not yet understood. Whether paraglobulin plays any part directly in the formation of fibrin or not, is still an open question.

V. **Amyloid** is a pathological product, occurring in fine grains, resembling starch-granules in appearance, in the membranes of the brain and cord, in waxy and lardaceous liver, and in the walls of the blood-vessels. Its composition is that of the albuminoids, from which it differs in being colored red by iodine; violet or blue by iodine and sulphuric acid. Soluble in hydrochloric acid with formation of syntonin; and in alkalies. It is not attacked by the gastric juice, and is not as prone to putrefaction as the albuminoids.

VI. **Collagen.**—Bony tissue is made up mainly of tricalcic phosphate, combined with an organic material called *ossein*, which is a mixture of collagen, elastin, and an albuminoid existing in the bone-cells. Collagen also exists in all substances which, when treated with water under the influence of heat and pressure, yield gelatin. It is insoluble in cold water, but by prolonged boiling is converted into gelatin, which dissolves. It is dissolved by alkalies.

Gelatin, obtained as above, from ossein, exists in the commercial product of that name, and in a less pure form in glue. When pure it is an amorphous, translucent, yellowish, tasteless substance, which swells up in cold water, without dissolving, and forms, with boiling water, a thick, sticky solution, which on cooling becomes, according to its concentration, a hard glassy mass or a soft jelly—the latter, even when the solution is very dilute. It is insoluble in alcohol and ether, but soluble, on warming, in glycerin; the solution in the last-named liquid forms, on cooling, a jelly which has recently been applied to various contrivances for copying writing. A film of gelatin impregnated with potassium dichromate becomes hard and insoluble on exposure to sunlight—a property which has been utilized in photography.

Elastin is obtained from elastic tissues by successive treatment with boiling alcohol, ether, water, concentrated acetic acid, dilute potash solution and water. It is fibrous, yellowish; swells up in water and becomes elastic; soluble with a brown color in concentrated potash solution. It contains no sulphur, and on boiling with sulphuric acid yields glycocol.

Chondrigen, a substance closely resembling collagen, existing in the cartilage and the tissues of lower animals, which differs from collagen in yielding chondrin when heated with water, under pressure.

Chondrin is distinguished from gelatin by being precipitated by almost all acids, including acetic; in not precipitating with tannin; and in yielding leucin in place of glycocol on boiling with sulphuric acid.

Keratin is the organic basis of horny tissues, hair, nails, feathers, whalebone, epithelium, tortoise-shell, etc. It is probably not a distinct chemical compound, but a mixture of several closely related bodies.

Mucin is a substance resembling the albuminoids, but containing no sulphur and existing in the different varieties of mucus, in certain pathological fluids, in the bodies of molluscs, in the saliva, bile, etc. Its solutions, like the fluids in which it occurs, are viscid. It is precipitated by acetic acid and by nitric acid, but is dissolved by an excess of the latter; it dissolves readily in alkaline solutions, and swells up in water, with which it forms a false solution. It is not coagulated by heat.

SOLUBLE ANIMAL FERMENTS.

Under this head are classed substances which are closely related to the albuminoids, which exist in animal fluids, and which have the power of effecting peculiar changes in other organic substances. Prominent among them are *ptyalin*, *pepsin*, and *pancreatin*.

Ptyalin is a substance closely resembling diastase in its characters and properties, existing in saliva. Like diastase, it converts starch into sugar.

Pepsin is the albuminoid ferment of the gastric juice. Attempts to separate it without admixture of other substances have hitherto proved fruitless; nevertheless, mixtures containing it and exhibiting its characteristic properties more or less actively, have been obtained by various methods. The most simple is that of Wittich, which consists in macerating the finely divided mucous membrane of the stomach in alcohol for forty-eight hours, and afterward extracting it with glycerin; this forms a solution of pepsin, which is quite active and resists putrefaction well, and from which a substance containing the pepsin is precipitated by a mixture of alcohol and ether.

If pepsin is required in the solid form, it is best obtained by Brücke's method. The mucous membrane of the stomach of the pig is cleaned and detached from the muscular coat by scraping; the pulp so obtained is digested with dilute phosphoric acid at 38°, until the greater part of it is dissolved; the filtered solution is neutralized with lime-water; the precipitate is collected, washed with water, and dissolved in dilute hydrochloric acid; to this solution a saturated solution of cholesterin, in a mixture of four parts alcohol and one part ether, is gradually added; the deposit so formed is repeatedly shaken with the liquid, collected on a filter, washed with water and then with dilute acetic acid, until all hydrochloric acid is removed; it is then treated with ether and water: the former dissolves cholesterin and is poured off, the latter the pepsin; after several shakings with ether the aqueous liquid is evaporated at 38°, when it leaves the pepsin as an amorphous, grayish white substance; almost insoluble in pure water, readily soluble in acidulated water, probably forming a compound with the acid, which possesses the property of converting albuminoids into peptones.

The so-called *pepsina porci* is either the calcium precipitate obtained as described in the first part of the above method; or, more commonly, the mucous membrane of the stomach of the pig, scraped off, dried, and mixed with rice-starch.

Pancreatin.—Under this name, substances obtained from the pancreatic secretion, and from extracts of the organ itself, have been described, and to some extent used therapeutically. They do not, however, contain all the ferments of the pancreatic juice, and in many instances are inert albuminoids. The actions of the pancreatic juice are various: 1st, it rapidly converts starch, raw or hydrated, into sugar; 2d, in alkaline solution—its natural reaction—it converts albuminoids into peptones; 3d, it emulsifies neutral fats; 4th, it decomposes fats, with absorption of water and liberation of glycerin and fatty acids.

The pancreatic secretion probably contains a number of ferments—certainly two, probably three. The one of these to which it owes its peptone-forming power has been obtained in a condition of comparative

purity by Kühne, and called by him *trypsin;* in aqueous solution it digests fibrin almost immediately, but it exerts no action upon starch.

The diastatic (sugar-forming) ferment of the pancreatic juice has not been separated, although a glycerin extract of the finely divided pancreatic tissue contains it, along with trypsin.

ANIMAL COLORING MATTERS.

Hæmoglobin and its derivatives. — *Hæmato-crystallin.* — The coloring matter of the blood is a highly complex substance, resembling the albuminoids in many of its properties, but differing from them in being crystallizable and in containing iron.

It exists in the red corpuscles, from which it is obtained by the following method: the blood is allowed to coagulate in a capsule and to remain at rest for twenty-four hours; the serum is decanted, the clot washed with water, cut into small pieces, and these again washed until the washings are not strongly precipitated by mercuric chloride; the clot is then extracted with water at 30°—40°, and the liquid filtered and collected in a cylinder surrounded with ice. A known fraction of the solution is treated with alcohol, gradually added from a burette during constant stirring of the solution, until a slight precipitate is formed; to the remainder of the aqueous liquid a somewhat smaller proportion of alcohol is then added than is required to form a precipitate; the mixture is placed in a freezing mixture, where, after some hours, an abundant crop of crystals separates; this is collected on a filter, washed first with water containing alcohol, and then with iced water, and finally dried below 0°.

Hæmoglobin exists in two conditions of oxidation; in the form in which it exists in arterial blood, and as obtained above, it is loosely combined with a certain quantity of oxygen, and is known as *oxyhæmoglobin.* The mean of many nearly concording analyses shows its composition to be $C_{600}H_{960}N_{154}FeS_3O_{179}$. When obtained from the blood of man and from that of many of the lower animals, it crystallizes in beautiful red prisms or rhombic plates; that from the blood of the squirrel in hexagonal plates; and that from the guinea-pig in tetrahedra. The crystals are always doubly refracting. It may be dried in vacuo at 0°; when it contains three to four per cent. of water of crystallization, which it loses at 110°—120°; if thoroughly dried below 0°, it may be heated to 100° without decomposition, but the presence of a trace of moisture causes its decomposition at a much lower temperature. Its solubility in water varies with the species of animal from whose blood it was obtained; thus, that from the guinea-pig is but sparingly soluble, while that from the pig is very soluble in water. It is also dissolved unchanged by very weak alkaline solutions, but is decomposed by acids or salts having an acid reaction.

Hæmoglobin, or *reduced hæmoglobin,* is formed from oxyhæmoglobin in the economy during the passage of arterial into venous blood, and by the action of reducing agents, or by boiling its solution at 40° in the vacuum of the mercury pump.

Oxyhæmoglobin is of a much brighter color than the reduced, and has a different absorption spectrum. The spectrum of oxyhæmoglobin has two bands between D and E; the one nearer D being the narrower, darker, and more sharply defined of the two, it is also the last to disappear on dilution; beyond a certain degree of concentration of the solution the two bands unite together, forming a single, broad, dark band,

extending beyond both D and E. The spectrum of hæmoglobin, on the other hand, has but one band, much broader and fainter than either of the oxyhæmoglobin bands, extending from D to about as near E as the border of the oxyhæmoglobin band nearest that line.

Hæmoglobin, in contact with oxygen or air, is immediately converted into oxyhæmoglobin. With carbon monoxide it forms a compound resembling oxyhæmoglobin in the color of its solution, but in which the carbon dioxide cannot be replaced by oxygen; for which reason hæmoglobin, once combined with carbon monoxide, becomes permanently unfit to fulfil its function in respiration. The spectrum of the carbon monoxide compound resembles somewhat that of oxyhæmoglobin, except that the bands are more nearly equal in width and intensity, and are rather nearer the violet end of the spectrum.

When a solution of oxyhæmoglobin is boiled, it becomes turbid, and a dirty, brownish red coagulum is deposited; the hæmoglobin has been decomposed into an albuminoid (or mixture of albuminoids), called by Preyer *globin*, and *hæmatin*. The latter, at one time supposed to be the blood-coloring matter, is a blue-black substance, having a metallic lustre and incapable of crystallization; it is insoluble in water, alcohol, ether, and dilute acids; soluble in alkaline solutions. It has the composition $C_{68}H_{70}N_8Fe_2O_{10}$ (?). Although itself uncrystallizable, hæmatin combines with hydrochloric acid to form a compound which crystallizes in rhombic prisms, and which is identical with the earliest known crystalline blood-pigment, *hæmin*, or Teichmann's crystals.

When reduced hæmatin is decomposed as above, in the absence of oxygen, hæmatin is not produced, but a substance identical with that called *reduced hæmatin*, and called by Hoppe-Seyler *hæmocromogen*.

Biliary pigments.—There are certainly four, and probably more, pigmentary bodies obtainable from the bile and from biliary calculi, some of which consist in great part of them.

Bilirubin, $C_{32}H_{36}N_4O_6$, is, when amorphous, an orange-yellow powder, and when crystalline, in red rhombic prisms. It is sparingly soluble in water, alcohol, and ether; readily soluble in hot chloroform, carbon disulphide, benzene, and in alkaline solutions. When treated with nitric acid containing nitrous acid, or with a mixture of concentrated nitric and sulphuric acids, it turns first green, then blue, then violet, then red, and finally yellow. This reaction, known as Gmelin's, is very delicate, and is used for the detection of bile-pigments in icteric urine and in other fluids.

Biliverdin, $C_{32}H_{36}N_4O_8$, is a green powder, insoluble in water, ether, and chloroform; soluble in alcohol and in alkaline solutions. It exists in green biles, but its presence in yellow biles or biliary calculi is doubtful. It responds to Gmelin's test. In alkaline solution it is changed after a time into biliprasin.

Bilifuscin, $C_{16}H_{20}N_2O_4$—obtained in small quantity from human gall-stones, is an almost black substance, sparingly soluble in water, ether, and chloroform; readily soluble in alcohol and in dilute alkaline solutions. Its existence in the bile is doubtful.

Biliprasin, $C_{16}H_{22}N_2O_6$ (?), exists in human gall-stones, in ox-gall, and in icteric urine. It is a black, shining substance, insoluble in water, ether, and chloroform; soluble in alcohol and in alkaline solutions.

Urobilin, or *hydrobilirubin*, $C_{32}H_{40}N_4O_7$. Under the name urobilin, Jaffé described a substance which he obtained from dark, febrile urine, and which he regarded as the normal coloring matter of that fluid; subse-

quently he obtained it from dog's bile and from human bile, from gall-stones and from fæces. *Stercobilin* from the fæces is identical with urobilin.

Urinary pigments.—Our knowledge of the nature of the substances to which the normal urinary secretion owes its color is exceedingly unsatisfactory. Jaffé in his discovery of urobilin shed but a transient light upon the question, as that substance has been found to exist in but a small percentage of the normal urines examined, although they certainly contain a substance readily convertible into it; a great deal of confusion has also been introduced into the subject by the description, especially by Thudichum, of ill-defined mixtures as urinary pigments. Besides the substance convertible into urobilin, and sometimes urobilin itself, human and mammalian urines contain at least one other pigmentary body: *uroxanthin*, or *indigogen*. This substance was formerly considered as identical with *indican*, a glucoside existing in plants of the genus *Isatis*, which, when decomposed, yields, among other substances, indigo-blue. Uroxanthin, however, differs from indican in that the former is not decomposed by boiling with alkalies, and does not yield any glucose-like substance on decomposition; the latter is almost immediately decomposed by boiling alkaline solutions, and, under the influence of acids and of certain ferments, yields, besides indigo blue, *indiglucin*, a sweet, non-fermentable substance, which reduces Fehling's solution.

Uroxanthin is a normal constituent of human urine, but is much increased in the first stage of cholera, in cases of cancer of the liver, Addison's disease, and intestinal obstruction. It has also been detected in the perspiration.

The presence of uroxanthin in the urine is indicated by the following tests: 1st, ten cubic centimetres of the urine are treated with an equal volume of hydrochloric acid, and then with a saturated solution of chloride of lime, added guttatim; the solution is colored, according to the amount of uroxanthin present, red, violet, green, or blue; on being filtered it leaves a blue deposit on the paper; 2d, three or four cubic centimetres of concentrated hydrochloric acid are placed in a test-tube, and thirty to forty drops of urine added; it assumes a red, violet, or blue color; 3d, the urine is warmed with two parts of nitric acid to 60°—70°, and shaken with chloroform; the latter fluid is colored violet-blue, and, if examined by the spectroscope, shows an absorption-band between C and D.

Melanin is the black pigment of the choroid, melanotic tumors, skin of the negro; and occurs pathologically in the urine, and deposited in the air-passages.

SILICON.

Si.....28

Also known as *silicium*, resembles carbon, and occurs in three allotropic forms: *Amorphous silicon*, formed when silicon chloride is passed over heated potassium or sodium, is a dark brown powder, heavier than water; when heated in air it burns with a bright flame to the dioxide. It dissolves in potash and in hydrofluoric acid, but is not attacked by other acids. *Graphitoid silicon* is obtained by fusing potassium fluosilicate with aluminium. It forms hexagonal plates, of sp. gr. 2.49, which do not burn when heated to whiteness in oxygen, but may be oxidized at that temperature by a mixture of potassium chlorate and nitrate. It dissolves slowly in alkaline solutions, but not in acids. *Crystallized silicon*, corresponding to the diamond, forms crystalline needles, which are only attacked by a mixture of nitric and hydrofluoric acids.

Silicon, although closely related to carbon, exists in nature in but few compounds; it has been caused to form artificial combinations, however, which indicate its possible capacity to exist in substances corresponding to those carbon compounds vulgarly known as organic, *e.g.*, *silicichloroform* and *silicibromoform*, $SiHCl_3$ and $SiHBr_3$.

Hydrogen silicide, SiH_4—is obtained as a colorless, insoluble, spontaneously inflammable gas, by passing the current of a galvanic battery of twelve cells through a solution of common salt, using a plate of aluminium, alloyed with silicon, as the positive electrode.

Silicon chloride, $SiCl_4$—a colorless, volatile liquid, having an irritating odor; sp. gr. 1.52; boils at 59°; formed when silicon is heated to redness in chlorine.

Silicic oxide—*Silicic anhydride*—*Silex*—SiO_2—is the most important of the compounds of silicon. It exists in nature in the different varieties of quartz, and in the rocks and sands containing that mineral, in agate, carnelian, flint, etc. Its purest native form is *rock crystal;* its hydrates occur in the opal, and in solution in natural waters. When crystallized it is fusible with difficulty; when heated to redness with the alkaline carbonates it forms *silicates*, which solidify to glass-like masses on cooling. It unites with water to form a number of acid hydrates. The normal hydrate, SiO_4H_4, has not been isolated, although it probably exists in the solution obtained by adding an excess of hydrochloric acid to a solution of sodium silicate. A gelatinous hydrate, soluble in water and in acids and alkalies, is obtained by adding a small quantity of hydrochloric acid to a concentrated solution of sodium silicate.

Hydrofluosilicic acid, SiF_6H_2—is obtained in solution by passing the gas disengaged by gently heating a mixture of equal parts of fluorspar and pounded glass, and six parts of sulphuric acid, through water, the disengagement tube being protected from moisture by a layer of mercury. It is used in analysis as a test for potassium and sodium.

VII. MOLYBDENUM GROUP.

MOLYBDENUM, Mo, 96; TUNGSTEN, W, 184; OSMIUM, Os, 200.

The position of this group is doubtful; osmium forms an oxide which is basic in character, and also exists in a sulphite, and it consequently belongs to the next class; nevertheless, the relations of its compounds to those of tungsten and molybdenum are such as to induce us to place it in the same group with them. It is probable that the lower oxides of tungsten and molybdenum will be found to possess basic characters, in which case the entire group should be transferred to the following class.

Molybdenum—isolated with difficulty by reduction of its oxides, which are obtained from a native sulphide.

Molybdic anhydride, MoO_3—unites with water to form a number of acids, the ammonium salt of one of which is a sensitive reagent for phosphoric acid. The conjugate *phosphomolybdic acid* is a valuable reagent for the alkaloids.

Tungsten— *Wolfram*—occurs associated with tin.

Tungstic anhydride, WO_3—a yellow powder which unites with water to form several acid hydrates, one of which, *metatungstic acid*, $W_4O_3H_2$, is used as a test for alkaloids, as are also the conjugate *silico-tungstic* and *phospho-tungstic acids*. *Sodium tungstate* is used to render fabrics non-inflammable.

Osmium is a rare element occurring with iridium in platinum ores. The oxide, OsO_4, known as *osmic acid*, is used as a staining agent in histological laboratories. Its vapor is intensely irritating.

CLASS III.

ELEMENTS WHOSE OXIDES UNITE WITH WATER, SOME TO FORM BASES, OTHERS TO FORM ACIDS. WHICH FORM OXYSALTS.

I. GOLD GROUP.

GOLD.....Au.....197

This, the only member of the group, forms two series of compounds: in one, AuCl, it is univalent; in the other, $AuCl_3$, trivalent. Its hydrate, *auric acid*, Au $(OH)_3$, corresponds to the oxide Au_2O_3. Its oxysalts are unstable.

It is yellow or red by reflected light, green by transmitted light, reddish purple when finely divided; not very tenacious; very malleable and ductile; softer than silver; fuses at about 1200°; sp. gr. 19.258 when cast, 19.367 when hammered.

It is not acted upon by water, air, oxygen, or single mineral acids. It combines directly with chlorine, bromine, iodine, phosphorus, antimony, arsenic, and mercury. It dissolves in nitro-muriatic acid. It is oxidized on contact of air by alkalies in fusion.

Aurous chloride, AuCl—a pale yellow, insoluble powder formed when auric chloride is heated to 200°; decomposed at higher temperatures into chlorine and gold.

Auric chloride—*Gold trichloride*—$AuCl_3$—obtained by dissolving gold in aqua regia, evaporating at about 100°, and purifying by crystallization from water. Deliquescent yellow prisms, very soluble in water, alcohol, and ether. Readily decomposed, with separation of gold, on contact with phosphorus or with reducing agents. Its solution, treated with the chlorides of tin, deposits the flocculent *purple of Cassius*. With the alkaline chlorides it forms permanent double chlorides—*chloraurates*. It stains the skin purple.

Sodium chloraurate and aurous iodide have been used medicinally. The trichloride is an active poison and a corrosive, being decomposed by organic matter with deposition of gold and liberation of chlorine.

Analytical characters.—*Hydrogen sulphide*—from neutral or acid solution; blackish brown precipitate in the cold; insoluble in nitric and hydrochloric acids, soluble in aqua regia and in yellow ammonium sulphydrate. *Stannous chloride*, with a little chlorine water, purple-red precipitate, insoluble in hydrochloric acid. *Ferrous sulphate*, brown deposit, which assumes the lustre of gold when dried and burnished.

II. IRON GROUP.

CHROMIUM, Cr, 52.4; MANGANESE, Mn, 55.2; IRON, Fe, 56.

These elements form two series of compounds; in one a single atom is divalent, as in $Fe''Cl_2$; in the other, two atoms combined form a hexavalent group, as in $(Fe)^{vi}Cl_6$. The oxides MO_3 are anhydrides, corresponding to which are acids and salts.

CHROMIUM.

Cr.....52.4

The element is isolated with difficulty from its oxide or chloride. It is steel-gray, hard, brilliant, magnetic at low temperatures; sp. gr. 6.8 at 20°. It combines with oxygen only at a red heat; is not attacked by acids, except hydrochloric acid; is readily attacked by alkalies.

Chromium sesquioxide—*Green oxide*—Cr_2O_3—is obtained, amorphous, by calcining a mixture of potassium dichromate and starch, or crystallized by heating neutral potassium chromate to redness in chlorine.

It is green; insoluble in water, acids, and alkalies; fusible with difficulty, and not decomposed by heat; not reduced by hydrogen. At a red heat in air, it combines with alkaline hydrates and nitrates to form chromates. It forms two series of salts, the terms of one of which are green, those of the other, violet. The alkaline hydrates separate a bluish green hydrate from solutions of the green salts, and a bluish violet hydrate from those of the violet salts.

Chromium green, or *emerald green*, is a brilliant green hydrate, formed by decomposing a double borate of chromium and potassium by water. It is used in the arts as a substitute for the arsenical greens, and is non-poisonous.

Chromic anhydride, CrO_3—improperly called *chromic acid*, is prepared by slowly adding one and one-half parts of strong sulphuric acid to one part of a concentrated solution of potassium dichromate, draining the crystals on a porous tile, and purifying by solution in water, exact precipitation by barium chromate, and crystallization over sulphuric acid.

It forms deliquescent, crimson prisms, very soluble in water, soluble in alcohol. It is a powerful oxidant, capable of igniting strong alcohol.

The true chromic acid has not been isolated, but salts corresponding to three acid hydrates are known: CrO_4H_2=*chromic acid;* $Cr_2O_7H_2$=*dichromic acid;* $Cr_3O_{10}H_2$=*trichromic acid.*

Chlorides.—Two chlorides and one oxychloride of chromium are known. *Chromous chloride*, $CrCl_2$, is a white solid, soluble with a blue color in water. *Chromic chloride*, $(Cr_2)Cl_6$, forms large, red crystals, insoluble in water when pure.

Sulphates.—A *violet* sulphate crystallizes in octahedra, $(SO_4)_3(Cr)_2$ +15 Aq., and is very soluble in water; at 100° it is converted into a *green* salt, $(SO_4)_3(Cr)_2$+5 Aq., soluble in alcohol, which at higher temperatures is converted into the red, insoluble, anhydrous salt. Chromic sulphate forms double sulphates, containing 24 Aq., with the alkaline sulphates (see Alums).

Analytical Characters.—Chromous Salts: *Potash*, brown precipitate; *Ammonium hydrate*, greenish white precipitate; *Alkaline sulphides*, black precipitate; *Sodium phosphate*, blue precipitate.

Chromic Salts.—*Potash*, green precipitate; excess of precipitant forms green solution, from which sesquioxide separates on boiling; *Ammonium hydrate*, greenish gray precipitate; *Ammonium sulphydrate*, greenish precipitate.

Chromates.—*Hydrogen sulphide*, in acid solution, brownish color, changing to green; *Ammonium sulphydrate*, greenish precipitate; *Barium chloride*, yellowish precipitate; *Silver nitrate*, brownish red precipi-

tate, soluble in nitric acid and in ammonia; *Lead acetate*, yellow precipitate, soluble in potash, insoluble in acetic acid.

Action on the economy.—*Chromic anhydride* oxidizes organic substances, and is used as a caustic.

The *chromates*, especially potassium dichromate (*q. v.*), are irritants, and have a distinctly poisonous action as well. Workmen handling the dichromate are liable to a form of chronic poisoning.

In acute chromium-poisoning, emetics, and subsequently magnesium carbonate in milk, are to be given.

MANGANESE.

Mn.....55.2

A grayish, brittle metal, hard, fusible with difficulty; sp. gr. 7.138—7.206; obtained by reduction of its oxides. When pure, it is not altered by dry air in the cold, but is superficially oxidized when heated. It decomposes water, especially when heated, and dissolves in dilute acids.

Oxides.—Manganese forms six oxides, or compounds representing them: *Manganous oxide*, MnO; *Manganoso-manganic oxide*, Mn_3O_4; *Manganic oxide*, Mn_2O_3; *Permanganic oxide*, MnO_2; *Manganic anhydride*, MnO_3; *Permanganic anhydride*, Mn_2O_7.

Permanganic Oxide.—*Manganese dioxide, Black oxide of manganese*, MnO_2, exists in nature as *pyrolusite*, the principal ore of manganese, in steel-gray or brownish, imperfectly crystalline masses.

At a red heat it loses 12 per cent. of oxygen, and is converted into Mn_3O_4, which, at a white heat, yields a further quantity of oxygen, leaving MnO. Heated with sulphuric acid, it gives off oxygen and forms manganous sulphate. With hydrochloric acid, it yields manganous chloride, water, and chlorine. With sulphuric and oxalic acids, it forms manganous sulphate, water, and carbon dioxide. It forms three hydrates, one of which corresponds to a series of salts, called *manganites*, $Mn_2O_{11}M_2$.

Neither *manganic anhydride*, nor *manganic acid*, MnO_4H_2, have been separated; they are, however, represented by well-defined salts, the *manganates*, MnO_4M_2.

Permanganic anhydride is an unstable, green liquid, and an active oxidant. *Permanganic acid*, MnO_4H, is obtained in solution by decomposition of its barium salt, by sulphuric acid (see Potassium permanganate).

Salts.—Like iron, manganese forms two series of salts: *Manganous salts*, containing Mn″; and *manganic salts*, containing $(Mn_2)^{vi}$; the former are colorless or pink, and soluble in water; the latter are quite unstable.

Manganous Sulphate, SO_4Mn.—is formed by the action of sulphuric acids upon the oxides of manganese. Below 6° it crystallizes with 7 Aq., and is isomorphous with ferrous sulphate; between 7° and 20° it forms crystals with 5 Aq., and is isomorphous with cupric sulphate; between 20° and 30° it crystallizes with 4 Aq. It is rose-colored, darker as the proportion of Aq. increases, soluble in water, insoluble in alcohol. With the alkaline sulphates it forms double salts with 6 Aq.

Analytical Characters.—Manganous.—*Potash.*—White precipitate, turning brown. *Alkaline carbonates*, white precipitate. *Ammonium sulphydrate*, flesh-colored precipitate, soluble in acids, sparingly

soluble in excess of precipitant. *Potassium ferrocyanide*, reddish white precipitate, soluble in hydrochloric acid. *Potassium ferricyanide*, brown precipitate. *Potassium cyanide*, rose-colored precipitate, forming brown solution in excess.

MANGANIC. — *Hydrogen sulphide*, precipitate of sulphur. *Ammonium sulphydrate*, flesh-colored precipitate. *Potassium ferrocyanide*, greenish precipitate. *Potassium ferricyanide*, brown precipitate. *Potassium cyanide*, light brown precipitate.

The MANGANATES are green salts, whose solutions are only stable in presence of excess of alkali, and turn brown when diluted and acidulated. The PERMANGANATES form red solutions, which are decolorized by reducing agents and by many organic substances; *sulphurous acid* turns them green.

IRON.

Fe.....56

The principal ores of iron are: *red hæmatite*, sesquioxide; *spathic ore*, ferrous carbonate; *bog ore*, ferrous carbonate, mixed with clay; *oölitic iron* and *brown hæmatite*, hydrates of the sesquioxide; *magnetic* or *black ore*, *pyrites*, and *meteoric iron*.

In working the ores, reduction is first effected in a *blast-furnace*, into which alternate layers of ore, coal, and limestone are fed from the top, while air is forced in from below. In the lower part of the furnace carbon dioxide is produced at the expense of the coal; higher up it is reduced by the incandescent fuel to carbon monoxide, which at a still higher point reduces the ore; the fused metal so liberated collects at the lowest point under a layer of *slag*, and is drawn off to be cast as *pig iron*. This product is then purified by burning out impurities in the process known as *puddling*.

Iron is used in the arts in three forms: *Cast iron*, a brittle, crystalline material, containing carbon, silicon, phosphorus, and sulphur. *Wrought iron*, a fibrous, tough variety, freed to a great extent from the impurities of cast iron, although not chemically pure. *Steel* is iron combined with a small quantity of carbon. It is prepared either by *cementation*, which consists of causing a pure iron to combine with carbon; or by the *Bessemer method*, which consists in burning the proper quantity of carbon out of cast iron. *Pure iron* is obtained by heating ferric oxide nearly to redness in a current of hydrogen; this is the *ferrum redactum* (U. S., Br.). The purest forms of commercial iron are those used in piano-strings, electro-magnets, and the teeth of carding-machines. The finely divided *iron by alcohol* is produced by mechanical division and levigation in alcohol.

Pure iron is quite soft; fuses at about 1600°; crystallizes in cubes or octahedra; is very tenacious; sp. gr. 7.25—7.9.

Iron is not altered by dry air at ordinary temperatures; at a red heat it is oxidized; in damp air it is converted into a hydrate, known as *rust*. *Tin plate* is sheet iron coated with tin; *galvanized iron* is protected by a coating of zinc. Iron unites directly with chlorine, bromine, iodine, sulphur, and the elements of the phosphorus group. Hydrochloric acid dissolves it as ferrous chloride, while hydrogen is liberated. Heated with strong sulphuric acid, it gives off sulphur dioxide; with the dilute

acid, hydrogen is given off and ferrous sulphate formed. Dilute nitric acid dissolves iron, but the concentrated acid renders it *passive*, when it is no longer attacked by a dilute acid until the passive condition is destroyed by contact with platinum, silver, or copper, or by heating to 40°.

Oxides.—Five oxides of iron are known, three of which are of interest.

FERROUS OXIDE, FeO—is formed by heating ferric oxide in carbon mon- or dioxide. Its hydrate, FeH_2O_2, is a greenish white substance, formed when a ferrous salt is decomposed by an alkaline hydrate.

FERRIC OXIDE—*Sesquioxide* or *Peroxide of iron*—Fe_2O_3.—When ferrous sulphate is heated, it turns white by loss of Aq.; then yellow, owing to formation of an oxyhydrate; then brick-red, when it has been converted into ferric oxide; another product being Nordhausen sulphuric acid.

Under the names *colcothar*, *red crocus*, *jeweller's rouge*, and *Venetian red*, it is used as a polishing material and as a pigment.

The *normal hydrate—Ferri peroxidum humidum* (U. S., Br.)—$(Fe_2)H_6O_6$—is a brown, gelatinous precipitate, formed when an alkali is added to a ferric salt. When dried at 100° it loses $2H_2O$, and is converted into *Ferri peroxidum hydratum* (U. S., Br.), $(Fe_2)O_2,H_2O_2$. Ferric hydrate is not precipitated in presence of fixed organic acids, or of sugar in sufficient quantity. Under water it is converted into an oxyhydrate, which is incapable of forming ferrous arsenate with arsenic trioxide.

A peculiar *modified ferric hydrate*, $(Fe_2)O_2H_2O_2$, is formed by drying the ordinary hydrate in vacuo and boiling it seven or eight hours in water; after washing, it is almost insoluble in nitric and hydrochloric acids, and gives no Prussian blue reaction; it dissolves in dilute acetic acid, the solution being reddish and appearing turbid by reflected light.

Recently precipitated ferric hydrate dissolves in solutions of ferric chloride or acetate, and the solutions, by dialysis, lose their acid, leaving in the dialyser a dark red solution of ferric hydrate. The *dialysed iron* so obtained is coagulated by heat, by sulphuric acid, alkalies, and many salts.

FERRIC ANHYDRIDE—Fe_2O_3, and FERRIC ACID—$Fe_2O_4H_2$, are unknown, but are represented by *potassium ferrate*, $Fe_2O_4K_2$.

Sulphides.—Eight sulphides of iron are known, of which three are of interest.

FERROUS SULPHIDE—*Protosulphide*—FeS—is formed: 1st, by bringing a mixture of sulphur and iron filings into a red-hot crucible; 2d, by pressing roll-sulphur upon white-hot iron; 3d, by precipitating a ferrous salt with an alkaline sulphydrate. The dry methods form brownish, brittle, fusible, magnetic masses; the wet method yields a black powder.

It is not decomposed by heat; is oxidized by damp air; is decomposed by dilute sulphuric acid, with formation of ferrous sulphate and hydrogen sulphide. It occurs in the fæces of persons taking chalybeate waters and preparations of iron.

FERRIC SULPHIDE—*Sesquisulphide*—Fe_2S_3—occurs in nature in *copper pyrites*, and is formed when the disulphide is heated to redness.

IRON DISULPHIDE—*Martial pyrites*—FeS_2—occurs in *yellow* and *white pyrites*, which are extensively used in the manufacture of sulphuric acid.

Chlorides.—Two chlorides of iron are known: $FeCl_2$ and $(Fe_2)Cl_6$.

FERROUS CHLORIDE, $FeCl_2$—is formed when iron is heated to redness in dry hydrochloric acid, or with sal-ammoniac, as an anhydrous, yellowish, crystalline, volatile, and very soluble substance. A hydrated compound, $FeCl_2+4Aq.$, is formed by solution of the anhydrous chloride, or by solution of iron in hydrochloric acid. It crystallizes in greenish, ob-

lique rhombic prisms; loses its water when heated without contact of air; heated in air it is converted into ferric chloride and an oxychloride.

FERRIC CHLORIDE—*Sesquichloride—Perchloride—Ferri chloridum* (U. S.)—Fe_2Cl_6—is obtained anhydrous by heating iron in chlorine; in violet, volatile, deliquescent plates. The hydrated compound, $Fe_2Cl_6+4Aq.$, is formed: 1st, by solution of the anhydrous; 2d, by dissolving iron in aqua regia; 3d, by dissolving hydrated ferric oxide in hydrochloric acid; 4th, by the action of chlorine or of nitric acid on solution of ferrous chloride; it is prepared pharmaceutically by the last method.

It forms yellow, nodular masses, or rhombic plates, very soluble in water, soluble in alcohol and ether. The *Liq. ferri chloridi* (U. S.), or *Liq. ferri perchloridi* (Br.), is an aqueous solution containing excess of acid. The *Tinct. ferri chloridi* (U. S.) is the liquor diluted with alcohol, and contains ethyl chloride and ferrous chloride.

Bromides.—These are similar in composition to the chlorides. *Ferrous bromide*, $FeBr_2$, is formed by the action of bromine on excess of iron in presence of water. *Ferric bromide*, Fe_2Br_6, is obtained by the action of excess of bromine on iron.

Iodides.—*Ferrous iodide—Ferri iodidum* (Br.)—FeI_2—is obtained with 4Aq., by adding iodine to excess of iron under warm water until the solution is pale green. *Ferric iodide*, Fe_2I_6, is formed by the action of excess of iodine on iron.

Salts.—FERROUS SULPHATE—*Protosulphate—Green vitriol—Copperas—Ferri sulphas* (U. S., Br.)—SO_4Fe—is obtained by oxidation of the sulphide remaining in the manufacture of sulphuric acid, and as a by-product in other processes. When required pure, it is prepared by dissolving iron in dilute sulphuric acid, and purifying by crystallization.

It crystallizes in oblique, rhombic prisms with 7 Aq.; it loses 6 Aq. at 100°, and the last Aq. at 300°; at a red heat it is decomposed into ferric oxide, and sulphur di- and trioxides. It is soluble in water, insoluble in alcohol. By exposure to air it is gradually converted into a basic ferric sulphate, $(SO_4)_3(Fe_2),5Fe_2O_3$.

FERRIC SULPHATES are quite numerous, and are formed by oxidation of ferrous sulphate under different conditions. The *normal sulphate*, $(SO_4)_3(Fe_2)$, is formed by treating ferrous sulphate solution with nitric acid, and evaporating after addition of one molecule of sulphuric acid for each two molecules of ferrous sulphate; its solution is the *Liq. ferri tersulphatis* (U. S.). Among the *basic sulphates* is one prepared by a process similar to the above, using half the quantity of sulphuric acid, which exists in *Liq. ferri subsulphatis* (U. S.), or *Monsel's solution*.

Ferric sulphate forms alums with the alkaline sulphates.

FERROUS NITRATE, $(NO_3)_2Fe$—a greenish, unstable salt, formed by double decomposition between barium nitrate and ferrous sulphate; or by the action of nitric acid on ferrous sulphide.

FERRIC NITRATES.—The *normal nitrate*, $(NO_3)_6(Fe_2)$, is formed along with ferrous nitrate by solution of iron in nitric acid. The *Liq. ferri nitratis* (U. S.), or *Liq. ferri pernitratis* (Br.), contains ferric nitrate, and is made with an acid of sp. gr. 1.115. It crystallizes in rhombic prisms with 18 Aq. or in cubes with 12 Aq. When iron is dissolved in nitric acid to saturation, basic nitrates are formed, which prevent crystallization of the normal salt.

TRIFERROUS PHOSPHATE, $(PO_4)_2Fe_3$—a white precipitate formed by adding disodic phosphate to a solution of a ferrous salt. By exposure to air it turns blue, a part being converted into ferric phosphate; the *ferri*

phosphas (U. S., Br.) is such a mixture of the two salts. It is insoluble in water, sparingly soluble in water containing carbonic and acetic acids.

A phosphate of iron, capable of turning blue, occurs in the lungs in phthisis, in blue pus, and in long-buried bones.

FERRIC PHOSPHATE, $(PO_4)_2(Fe_2)$—is formed by the action of an alkaline phosphate on ferric chloride. It is soluble in hydrochloric, nitric, citric, and tartaric acids; insoluble in phosphoric acid.

FERRIC PYROPHOSPHATE, $(P_2O_7)_3(Fe_2)_2$—is formed by decomposition of a ferric salt by sodium pyrophosphate; an excess of the sodium salt dissolves the precipitate when warmed, and on evaporation leaves scales of a double salt, $(P_2O_7)_3(Fe_2)_2$, $(P_2O_7)_2Na_8+20Aq$. A similar ammonium salt, accompanied by ferric citrate, exists in the *ferri pyrophosphas* (U. S.).

FERROUS ACETATE, $(C_2H_3O_2)_2Fe$—is formed by decomposition of ferrous sulphate by calcium acetate. It crystallizes in soluble, silky needles.

FERRIC ACETATES.—The *normal salt*, $(C_2H_3O_2)_6(Fe_2)$, is obtained by adding slight excess of ferric sulphate to lead acetate, and decanting after twenty-four hours. It is dark red, uncrystallizable, very soluble in alcohol and in water. If its solution be heated it darkens suddenly, gives off acetic acid, and contains a basic acetate; when boiled it loses all its acetic acid and deposits ferric hydrate; when heated in closed vessels to 100°, and treated with a trace of mineral acid, it deposits the modified ferric hydrate.

FERROUS CARBONATE, CO_3Fe—is obtained in the hydrated form by adding an alkaline carbonate to a ferrous salt; on exposure to air it turns red from formation of ferric hydrate. It is insoluble in pure water, but soluble in water containing carbonic acid, probably as a bicarbonate, in which form it exists in mineral waters. The *ferri carbonas saccharata* (Br.) is this salt, to which sugar is added to delay decomposition; the *ferri subcarbonas* (U. S.) is ferrous hydrate.

FERROUS LACTATE—*Ferri lactas* (U. S.)—$(C_3H_5O_3)_2Fe+3Aq$.—is formed by dissolving iron filings in lactic acid. It crystallizes in light yellow needles, soluble in water, insoluble in cold alcohol; permanent in air when dry.

FERROUS OXALATE—*Ferri oxalas* (U. S.)—$C_2O_4Fe+2Aq$.—is formed by dissolving iron in solution of oxalic acid. It is a bright yellow, crystalline powder, sparingly soluble in hot water.

FERROUS TARTRATE, $C_4H_4O_6Fe+2Aq$.—a white, crystalline powder, formed by dissolving iron in hot, strong solution of tartaric acid.

FERRIC TARTRATE, $(C_4H_4O_6)_3(Fe_2)+3Aq$.—a dirty yellow, amorphous mass, obtained by dissolving recently precipitated ferric hydrate in tartaric acid, and evaporating below 50°. Its solution is not precipitated by alkalies or alkaline carbonates.

A number of double tartrates, containing the group $(Fe_2O_2)''$ are also known. Such are: *Ferrico-ammonic tartrate; ferri et ammonii tartras* (U. S.), $(C_4H_4O_6)_2(Fe_2O_2)(NH_4)_2+4Aq$., and *Ferrico-potassic tartrate; ferri et potassii tartras* (U. S.), $(C_4H_4O_6)_2(Fe_2O_2)K_2$; they are prepared by dissolving recently precipitated ferric hydrate in hot solutions of the hydro-alkaline tartrate. They only react with ferro- and sulphocyanides after addition of a mineral acid.

FERRIC FERROCYANIDE—*Ferri ferrocyanidum* (U. S.)—*Prussian blue*—$(FeC_6N_6)_3(Fe_2)_2+18Aq$.—a dark blue precipitate formed when potassium ferrocyanide is added to a ferric salt. It is insoluble in water, alcohol, ether, and dilute acids; soluble in oxalic acid (blue ink); alkalies turn it brown.

FERROUS FERRICYANIDE—*Turnbull's blue*—($Fe_2C_{12}N_{12}$) Fe_3+_nAq.—a dark blue precipitate, produced by potassium ferricyanide with ferrous salts.

ANALYTICAL CHARACTERS.—FERROUS SALTS are acid, colorless when anhydrous, pale green when hydrated; oxidized by air to basic ferric compounds. *Potash*, greenish white precipitate, insoluble in excess, changing to brown in air. *Ammonium hydrate*, greenish precipitate, soluble in excess, not formed in presence of ammoniacal salts. *Ammonium sulphydrate*, black precipitate, soluble in acids. *Potassium ferrocyanide*, white precipitate, turning blue in air. *Potassium ferricyanide*, blue precipitate, soluble in potash, insoluble in hydrochloric acid.

FERRIC SALTS are acid, and yellow or brown. *Potash* or *ammonium hydrate*, voluminous, red-brown precipitate. *Hydrogen sulphide* in acid solution, milky deposit of sulphur, ferric reduced to ferrous compound. *Ammonium sulphydrate*, black precipitate. *Potassium ferrocyanide*, dark blue precipitate, insoluble in hydrochloric acid, soluble in potash. *Potassium sulphocyanate*, dark red color; prevented by tartaric and citric acids. *Tannin*, blue-black color.

III. ALUMINIUM GROUP.

GLUCINIUM	Gl	13.8	GALLIUM	Ga	69.9
ALUMINIUM	Al	27.5	INDIUM	In	113.4

This group is placed in the third class by virtue of the existence of the aluminates, and of the relations between the compounds of these elements and some of those of the previous groups. They form, however, but one series of compounds, corresponding to the ferric, containing the group $(M_2)^{vi}$. No acids or salts of the members of the group, other than aluminium, are known; yet their resemblances in other points are such as to forbid their separation.

ALUMINIUM.

Al..... 27.5

This, the only element of the group of practical importance, although very abundant in combination, was only isolated in 1817 by Woehler, by a method which has since become general for the separation of metals whose compounds are difficultly reducible, which consists in passing the vapor of the chloride over sodium heated to redness.

Aluminium is a bluish white metal; hard, very malleable and ductile when annealed from time to time; slightly magnetic; a good conductor of electricity; fuses at about 700°; non-volatile; sp. gr. 2.56 when cast, 2.67 when rolled. It is not affected by air or oxygen, except at very high temperatures, and even then very superficially. If, however, it contain silicon, it burns readily, forming aluminium silicate. Boron, silicon, and the elements of the chlorine group combine with it directly. It does not decompose water at a red heat. Hydrochloric acid, gaseous or in solution, attacks it, hydrogen is given off, and aluminium chloride formed. It dissolves readily in alkaline solutions with liberation of hydrogen and formation of aluminates. It unites with copper to form a

golden yellow alloy, known as *aluminium bronze.* The great toughness and lightness of aluminium and of its alloys render it valuable for the manufacture of metallic objects where lightness is desirable.

Aluminium oxide—*Alumina*—Al_2O_3—exists in nature, nearly pure, in *corundum*, *emery*, *ruby*, *sapphire*, and *topaz.* It is obtained artificially by calcining the hydrate, and is also formed when ammonia alum (*q. v.*) is calcined at a red heat. It is a light, white, odorless, tasteless powder, fuses with difficulty, and, on cooling, forms crystals which are hard enough to scratch glass. Unless it have been heated beyond dull redness, it combines with water, the union being attended with liberation of heat. It is attacked with great difficulty by acids, its best solvent being sulphuric acid diluted with its weight of water. It also dissolves with difficulty in alkaline solutions, but combines with fused potash and soda to form aluminates. It is not reduced by charcoal.

Aluminium hydrate, $Al_2H_6O_6$—is formed when a solution of an aluminium salt is precipitated by ammonium hydrate or carbonate. It forms a gelatinous precipitate which, when washed and dried, leaves an amorphous, translucid mass. When it is formed in the presence of coloring matters, these are mechanically carried down with it, and the dried deposits are used as pigments, known as *lacs;* it is insoluble in water when freshly precipitated; soluble in acids and solutions of the fixed alkalies. With the acids it forms salts of aluminium; and with the alkalies, aluminates of the alkaline element. When heated to near redness it is decomposed into aluminium oxide and water. A soluble variety of alumina has been obtained by dialysing a solution of alumina in aluminium chloride solution, or by heating for 240 hours a dilute solution of aluminium acetate.

Aluminates are for the most part crystalline, soluble compounds, obtained by the action of metallic oxides or hydrates upon alumina. *Potassium aluminate,* $Al_2O_4K_2+3Aq.$—is formed by dissolving recently precipitated aluminium hydrate in potash solution. It forms white crystals; very soluble in water, insoluble in alcohol; caustic and alkaline. By a large quantity of water it is decomposed into aluminium hydrate and a more alkaline salt, $Al_2O_3K_2$. *Sodium aluminate.*—The aluminate $Al_2O_4Na_2$ is not known. That having the composition $Al_4O_8Na_8$ is prepared industrially, for use in dyeing, by heating to redness a mixture of one part of sodium carbonate and two parts of a native, ferruginous aluminium hydrate (beauxite). It is insoluble in water, and is decomposed by carbonic acid with precipitation of aluminium hydrate.

Aluminium chloride, Al_2Cl_6—is prepared industrially as a step in the manufacture of aluminium. It crystallizes in colorless, hexagonal prisms; fusible; volatile; deliquescent; very soluble in water and in alcohol. From a hot, concentrated solution it separates in prisms containing 12 Aq. It absorbs hydrogen sulphide, hydrogen phosphide, and ammonia, with which it forms compounds.

An impure solution of aluminium chloride is used as a disinfectant under the name *chloralum.*

Salts.—Aluminium Sulphates, $(SO_4)_3Al_2+18Aq.$—is prepared artificially on a large scale from kaolin. It is also formed (*Aluminii sulphas,* U. S.) by dissolving aluminium hydrate in moderately diluted sulphuric acid.

It crystallizes with difficulty in thin, flexible plates; soluble in water, very sparingly soluble in alcohol. When heated, it fuses in its water of crystallization, which it gradually loses up to 200°, when a white, amor-

phous powder of the anhydrous salt, $(SO_4)_3Al_2$, remains; this at a red heat is decomposed, leaving a residue of pure alumina.

Alums are double sulphates of the alkaline metals, and the higher sulphates of the elements of this and the preceding group. When crystallized, they contain 24 Aq., and have the general formula: $(SO_4)_2(M_2)^{VI}$, $SO_4R'_2+24Aq.$, in which (M_2) may be (Fe_2), (Mn_2), (Cr_2), (Al_2), or (Ga_2); and R_2 may be K_2, Na_2, Rb_2, Cs_2, Tl_2, or $(NH_4)_2$. They are isomorphous.

The substance formerly known as *alum* is the double sulphate of aluminium and potassium, $(SO_4)_3Al_2$, SO_4K_2+24Aq. It is manufactured from aluminous schists, from clays free from iron, and from *aluminite*, a native subsulphate of aluminium and potassium. That from the last-named source crystallizes in cubes, and is known as *cubic* or *Roman alum*. It is formed when concentrated solutions of sulphates of aluminium and of potassium are mixed in suitable proportions.

It crystallizes in large, transparent, regular octahedra; has a sweetish, astringent taste; 100 parts of water at 10° dissolve 9.52 parts of alum; and at 100°, 357.48 parts. When heated to about 92°, it fuses in its water of crystallization, and gradually loses 45.5 per cent. of its weight of water as it is heated to a temperature near redness. The product, which is readily pulverizable, and slowly but completely soluble in 20—30 times its weight of water, is known as *burnt alum*, and is the anhydrous double sulphate. At a bright red heat, sulphur dioxide and oxygen are given off, and alumina and potassium sulphate remain. At a higher temperature, potassium aluminate is formed. Its solutions, acid in reaction, deposit aluminium hydrate when neutralized with ammonium hydrate.

Potash alum is giving place in the arts to the cheaper *aluminium and ammonium sulphate*, or *ammonia alum*, $(SO_4)_3Al_2$, $SO_4(NH_4)_2+24Aq.$, which differs from potash alum in being more soluble between 20° and 30°, and less soluble in colder or warmer water, and in the manner in which it is affected by heat. It fuses in its water of crystallization, as does potash alum; at about 205°, the temperature reached in making *burnt alum*, it loses its ammonium sulphate, leaving a white, hygroscopic substance, very slowly and incompletely soluble in water; when more strongly heated, it leaves alumina.

Alum and the alkaline bicarbonates decompose each other with formation of aluminium hydrate, an alkaline sulphate, and carbon dioxide, a reaction utilized in alum baking-powders (*q. v.*).

Silicates are very abundant in the different varieties of *clay*, *feldspar*, *albite*, *labradorite*, *mica*, etc. The clays are hydrated aluminium silicates, more or less contaminated with alkaline and earthy salts and iron, to which last certain clays owe their color. The purest is *kaolin*, or porcelain clay, a white or grayish powder. They are largely used in the manufacture of the different varieties of bricks, terra cotta, pottery, and porcelain. *Porcelain* is made from the purer clays, mixed with sand and feldspar; the former to prevent shrinkage, the latter to bring the mixture into partial fusion, and to render the product translucent. The fashioned articles are subjected to a first baking; the porous, baked clay is then coated with a *glaze*, usually composed of oxide of lead, sand, and salt. During a second baking, the glaze fuses and coats the article with a hard, impermeable layer. The coarser articles of pottery are glazed by throwing sodium chloride into the fire; the salt is volatilized, and, on contact with the hot aluminium silicate, deposits a coating of the fusible sodium silicate, which hardens on cooling.

ALUMINIUM ACETATE, $(C_2H_3O_2)_6(Al_2)$—is obtained only in solution, by decomposing a concentrated solution of aluminium sulphate with lead acetate, or by dissolving aluminium hydrate in acetic acid. It is an uncrystallizable liquid, having a styptic taste, which is decomposed when heated or on standing, with formation of basic acetates. Is extensively used in dyeing.

Analytical Characters.—*Potash* or *soda*, white precipitate, soluble in excess; *Ammonium hydrate*, white precipitate, almost insoluble in excess, especially in the presence of ammoniacal salts; *Sodium phosphate*, white precipitate, readily soluble in potash and soda, but not in ammonium hydrate; readily soluble in mineral acids, but not in acetic acid; *Blowpipe;* on charcoal does not fuse, and, when moistened with solution of cobalt nitrate, turns dark sky-blue.

V. LEAD GROUP.

LEAD.....Pb.....207

This element is usually classed with cadmium, bismuth, or copper and mercury; it differs, however, from bismuth in being divalent or quadrivalent, but not trivalent, and in forming no compounds resembling those of bismuthyl (BiO); from cadmium in the nature of its oxygen compounds; and from mercury and copper in forming no compounds similar to the mercurous and cuprous salts. Indeed, the nature of the lead compounds is such that the element is best classed in a group by itself, which finds a place in this class by virtue of the existence of potassium plumbate.

The most abundant ore of lead is a sulphide known as *galena*, which is worked for lead and silver. The ore is roasted; the mixture of oxide, sulphide and sulphate so formed is heated in a reverberatory furnace, to yield an impure metal, called *work-lead*. If the ore be rich in silver, it is subjected to refining by crystallization and cupellation. At first, the work-lead is fused and allowed to cool slowly; crystals of lead separate and are removed, while the silver remains in the more fusible alloy. After several crystallizations, the concentrated alloy is fused in the cupelling furnace and a powerful current of air is driven over the surface of the molten metal; the lead is thus oxidized and is driven off by the current of air through a notch, whose depth is increased as the operation proceeds. As the last film of lead oxide is carried off, the clear surface of the fused silver is exposed and the mass *brightens*, indicating the termination of the operation.

Lead is a grayish white metal; brilliant upon freshly cut surfaces, very soft and pliable, not very malleable or ductile, fuses at 334°, and, on cooling, crystallizes in octahedra; a poor conductor of electricity; a better conductor of heat. When expanded by heat, it does not, on cooling, return to its original volume.

Lead, when exposed to air, is oxidized; it is not acted on by pure water, deprived of air; by the combined action of air and water, lead is oxidized to the hydrate, PbH_2O_2, which dissolves to an appreciable extent. The solvent action of water upon lead is increased, owing to the formation of basic salts, by the presence of nitrogenized organic matters, nitrates, and nitrites; on the other hand, carbonates, sulphates, and carbon dioxide, by their tendency to form insoluble coatings, diminish the

solubility of the metal in water. Nitric acid dissolves lead readily; sulphuric acid, when cold, does not affect it; but when heated, dissolves it the more readily the more concentrated the acid. Hydrochloric acid of sp. gr. 1.12 attacks it, especially if heated.

Several alloys of lead are used in the arts: Type-metal=lead and antimony; pewter=lead and tin; plumber's solder=lead and tin.

Oxides.—Lead forms five oxides: Pb_2O, PbO, Pb_3O_4, Pb_2O_3, and PbO_2.

Lead Monoxide—*Protoxide—Massicot—Litharge—Plumbi oxidum* (U. S., Br.)P—bO is prepared by calcining lead or its carbonate or nitrate. If the product have been fused, it is *litharge;* if not, *massicot;* the two varieties differing in color and in texture, but not in composition. Massicot is prepared by calcining lead and removing the pellicle as soon as it is formed; litharge, by fusing massicot, and allowing it to cool. When fused, it crystallizes in mica-like plates; from its solution in soda or potash, it is deposited in white, rhombic dodecahedra or in rose-colored cubes. It fuses at a heat approaching redness; it volatilizes at a white heat; sp. gr. 9.277; after fusion, 9.5. It is sparingly soluble in water, the solution being alkaline in reaction.

When heated to 300° in contact with air, it is oxidized to minium. When fused in earthen crucibles it forms a fusible silicate, and thus perforates the vessel. It is readily reduced by charcoal or hydrogen. Chlorine converts it into the chloride with separation of oxygen. It is a powerful base; it decomposes the alkaline salts with liberation of the alkali; it dissolves readily in nitric acid and in hot acetic acid, with formation of nitrate or acetate. When rubbed up with oils it decomposes the glyceric ethers, and combines with the fatty acids to form lead-soaps; one of which, the oleate, is the *emplastrum plumbi* (U. S., Br.). It also combines with the alkalies and earths to form *plumbites. Calcium plumbite,* Pb_2O_2Ca, is a crystalline compound, formed by heating litharge with milk of lime. Its solution is used as a hair-dye.

Plumboso-plumbic Oxide—*Red oxide of lead—Minium—Red lead*—Pb_3O_4 or PbO_2, 2PbO or $PbO_2Pb+PbO$—is prepared for use as a pigment, and in the manufacture of glass, by heating litharge to 300° in contact with air. It ordinarily has the composition given above, and has been considered as composed of one molecule of the dioxide combined with two of the monoxide; or as the lead salt of plumbic acid combined with a molecule of the monoxide. An orange-colored variety is formed by heating lead carbonate to 300°.

It is a brilliant red powder, sp. gr. 8.62. When strongly heated it is converted into litharge; a change which is also brought about by reducing agents. Nitric acid changes its color to brown, dissolving the monoxide and leaving the dioxide. Hydrochloric acid decomposes it with formation of chlorine, lead chloride, and water.

The commercial product is frequently contaminated with oxide of iron and brick-dust. It should dissolve in dilute nitric acid to which a fragment of sugar has been added.

Lead Dioxide—*Peroxide of lead—Puce oxide of lead—Binoxide of lead—Plumbic anhydride*—PbO_2—is prepared either by dissolving the monoxide out of minium by dilute nitric acid, or by passing a current of chlorine through water holding lead carbonate in suspension.

It is a dark, reddish brown powder, sometimes crystalline; sp. gr. 8.903 to 9.190; insoluble in water. When heated it loses half its oxygen and is converted into the monoxide. It is a valuable oxidizing agent. It absorbs sulphur dioxide to form lead sulphate.

PLUMBIC ACID, PbO_3H_2—is formed in crystalline plates, at the positive pole, when alkaline solutions of the lead salts are decomposed by a weak current.

The alkalies dissolve lead dioxide to form well-defined but unstable salts, called *plumbates*. *Potassium plumbate*, $PbO_3K_2+3Aq.$, is obtained in cubic crystals when lead dioxide is gently heated in a silver vessel with concentrated potash solution. It is decomposed by water.

Lead Sulphide, PbS—exists in nature in cubic crystals as the chief ore of lead, *galena*. It is also formed by direct union of the elements; by heating lead monoxide with sulphur or vapor of carbon disulphide; or by decomposing a solution of a lead salt with hydrogen sulphide or an alkaline sulphydrate.

The native sulphide is bluish gray and has a metallic lustre; sp. gr. 7.58; that obtained by precipitation is a black powder of sp. gr. 6.924. It fuses at a red heat and is partially sublimed, partially converted into a subsulphate with loss of sulphur. When heated in air it is converted into sulphate and oxide, and sulphur dioxide. Heated in hydrogen it is reduced. Hot nitric acid oxidizes it to the sulphate; hot hydrochloric acid converts it into the chloride; boiling sulphuric acid converts it into the sulphate and disengages sulphur dioxide.

Chlorides.—Two compounds of chlorine and lead are known, $PbCl_2$ and $PbCl_4$.

LEAD CHLORIDE, $PbCl_2$—is formed by the action of chlorine upon lead at a red heat by the action of boiling hydrochloric acid upon the metal; and by double decomposition between a soluble salt of lead and a chloride. In the last case, if the solutions be cold and not too dilute, the chloride is precipitated.

It crystallizes in plates or in silky, hexagonal needles; soluble in 135 parts of water at 12.5°; less soluble in water containing hydrochloric acid; more soluble in concentrated hydrochloric acid and in boiling water.

Lead also forms several oxychlorides; that having the composition $PbCl_2,7PbO$ is used as a pigment, and is known as *Cassel*, *Paris*, *Verona*, or *Turner's yellow*.

Iodide—*Plumbi iodidum* (U. S., Br.)—PbI_2—is deposited as a bright yellow powder when a solution of potassium iodide is added to a solution of a lead salt. It is almost insoluble in cold water, sparingly soluble in boiling water. When fused in air it loses iodine and is converted into an oxysalt. When exposed to light and moisture it is decomposed with liberation of iodine. It dissolves in solutions of ammonium chloride, sodium hyposulphite, alkaline iodides, and potassium hydrate.

Salts.—NITRATES.—Besides a neutral salt, lead forms basic nitrates, some of which seem to indicate the existence of nitrogen acids similar to those of phosphorus.

$(NO_4)_2Pb_3$, Lead orthonitrate.....$(PO_4)_2Pb_3$, Lead orthophosphate.
$N_2O_7Pb_2$, Lead pyronitrate.....$P_2O_7Pb_2$, Lead pyrophosphate.
$(NO_3)_2Pb$, Lead metanitrate.....$(PO_3)_2Pb$, Lead metaphosphate.

Neutral lead nitrate—*Plumbi nitras* (U. S., Br.)—$(NO_3)_2Pb$—is formed by solution of lead or its oxides in excess of nitric acid. It forms anhydrous crystals, soluble in 1.98 parts water at 17.5°, and in 0.7 parts at 100°. It is decomposed by heat, with liberation of nitrogen tetroxide.

SULPHATES.—The *neutral sulphate*, SO_4Pb—is formed by the action of hot concentrated sulphuric acid on lead; or, by double decomposition

between a sulphate and a lead salt in solution. It is a white powder, almost insoluble in water; soluble in concentrated sulphuric acid, from which it is deposited on dilution.

CHROMATES.—The *neutral chromate*, CrO_4Pb—is formed by precipitating lead nitrate with potassium chromate, and is used as a pigment, *chrome yellow*. It is insoluble in water; soluble in alkalies.

ACETATES.—The *Neutral acetate—Salt of Saturn—Sugar of lead—Plumbi acetas*—$(C_2H_3O_2)_2Pb+3Aq.$—is prepared by dissolving litharge in acetic acid; or, by exposing lead in contact with acetic acid to the atmosphere, evaporating and crystallizing.

It crystallizes in large, oblique, rhombic prisms, sweetish, with a metallic after-taste; soluble in 1.5 parts cold water and in 8 parts alcohol. The solutions are acid. By exposure to the air it effloresces upon the surface and is superficially converted into carbonate. It fuses at 75.5°; loses Aq. and a part of its acid to 100°, forming the sesquibasic acetate. At 280° it enters into true fusion, and at a slightly higher temperature is decomposed into carbon dioxide, acetone, and lead. Its aqueous solution dissolves litharge, with formation of basic acetates.

Of the subacetates, that having the composition $(C_2H_3O_2)PbOH, 2PbO$, the *sexbasic acetate*, is the only one requiring mention. It is the main constituent of *Liq. plumbi subacetatis* (U. S., Br.), or *Goulard's extract*, obtained by boiling a solution of the neutral acetate with lead monoxide in fine powder. This solution becomes milky when added to ordinary water, by formation of lead sulphate and carbonate.

LEAD CARBONATE—*Plumbi carbonas* (U. S., Br.)—CO_3Pb—is formed by double decomposition between a carbonate and a salt of lead in solution, or by passing carbon dioxide through a solution containing lead. It is a white powder, sp. gr. 6.43; insoluble in water.

Besides the neutral salt there exist several basic carbonates which occur in varying proportions in the commercial product known as *ceruse* or *white lead*. This is prepared by several processes. In the *Clichy process*, which is that usually adopted, litharge is dissolved in lead acetate solution, and the subacetate thus produced is decomposed by a current of carbon dioxide, the neutral acetate being regenerated and used again.

White lead is used in oil-painting, forming a part of all but the darkest pigments. The darkening of lead whites by exposure to air is due to the presence of traces of hydrogen sulphide in the atmosphere. The regeneration of oil-paintings dimmed by atmospheric action is accomplished by oxygenated water, which oxidizes the dark sulphide to the white sulphate.

Analytical characters.—*Hydrogen sulphide* in acid solution; a black precipitate, insoluble in acids and in alkaline sulphides. *Ammonium sulphydrate;* black precipitate, insoluble in excess. *Hydrochloric acid*; white precipitate, soluble in boiling water, from which it crystallizes on cooling; not altered in appearance by ammonium hydrate. This reaction does not occur in dilute solutions. *Ammonium hydrate;* white precipitate, insoluble in excess. *Potassium hydrate;* white precipitate, soluble in excess, especially when heated. *Sulphuric acid* or *sulphate;* white precipitate, insoluble in weak acids, soluble in solution of ammonium tartrate. *Potassium iodide;* yellow precipitate, sparingly soluble in boiling water, soluble in a large excess of the reagent. *Potassium chromate;* yellow precipitate, soluble in potash solution. *Iron* or *zinc* separate the element from solutions of its salts.

Action on the economy.—All of the soluble compounds of lead and those which, although not soluble, are readily convertible into solu-

ble compounds by water, air, or the digestive fluids, are actively poisonous. Some are also injurious by their local action upon the tissues with which they come in contact; such are the acetate, and, in a less degree, the nitrate.

The *chronic* form of lead intoxication, *painter's colic, etc.*, is purely poisonous, and is produced by the continued absorption of minute quantities of lead, either by the skin, lungs, or stomach. The acute form presents symptoms referable to the local as well as to the poisonous action of the lead salt, and is usually caused by the ingestion of a single dose of the acetate or carbonate.

Metallic lead, although probably not poisonous of itself, causes chronic lead-poisoning by the readiness with which it is converted into compounds capable of absorption. The sources of poisoning by metallic lead are: the contamination of drinking water which has been in contact with the metal (see p. 56); the use of articles of food or of chewing tobacco which has been packed in tin-foil containing an excess of lead; the drinking of beer or other beverages which have been in contact with pewter; or the handling of the metal and its alloys.

Almost all the compounds of lead may produce painter's colic. The carbonate, in painters, artists, manufacturers of white lead, and in persons sleeping in newly painted rooms; the oxides, in the manufacturers of glass, pottery, sealing-wax, and litharge, and by the use of lead-glazed pottery; by other compounds, by the inhalation of the dust of cloth factories, and by the use of lead hair-dyes.

Acute lead-poisoning is by no means of as common occurrence as the chronic form, and usually terminates in recovery. It is caused by the ingestion of a single large dose of the acetate, subacetate, carbonate, or of red lead. In such cases the administration of magnesium sulphate is indicated; it enters into double decomposition with the lead salt to form the insoluble lead sulphate.

Lead once absorbed is eliminated very slowly, it becoming fixed by combination with the albuminoids, a form of combination which is rendered soluble by potassium iodide. The channels of elimination are by the perspiration, urine, and bile.

In the analysis for mineral poisons (see p. 128), the major part of the lead is precipitated as sulphide in the treatment by sulphuretted hydrogen. The lead sulphide remains upon the filter after extraction with ammonium sulphydrate; it is treated with warm hydrochloric acid, which decolorizes it by transforming the sulphide to chloride. The lead chloride thus formed is dissolved in hot water, from which it crystallizes on cooling. The solution still contains lead chloride in sufficient quantity to respond to the tests for the metal.

Although lead is not a normal constituent of the body, the every-day methods in which it may be introduced into the economy, and the slowness of its elimination are such as to render the greatest caution necessary in drawing conclusions from the detection of lead in the body after death.

VI. BISMUTH GROUP.

BISMUTH.....Bi.....210

This element is usually classed along with antimony: by the older authors among the metals, and by the more modern in the phosphorus group of metalloids. We are led, however, to rank bismuth in our third

class and in a group alone, because: 1st, while the so-called salts of antimony are not salts of the element, but of the radical antimonyl $(SbO)'$, bismuth enters into saline combination, not only in the radical bismuthyl, $(BiO)'$, but also as an element, as in the nitrate $(NO_3)_3Bi$; 2d, while the compounds of the elements of the nitrogen group in which those elements are quinquivalent, are, as a rule, more stable than those in which they are trivalent, only one compound of bismuth is known in which that element is quinquivalent, and that one is a very unstable acid; 3d, the hydrates of the nitrogen group are strongly acid and their corresponding salts are stable and well-defined; but those hydrates of bismuth which are acid are but feebly so, and the bismuthates are formed with difficulty and are unstable; 4th, no hydrogen compound of bismuth is known.

Bismuth crystallizes in rhombohedra; has a brilliant, metallic lustre, with bluish and reddish reflections; is hard and brittle; fuses at 247°; sp. gr. 9.935 when crystallized, 9.677 when annealed.

It is only superficially oxidized in cold air; heated to redness in air, it becomes coated with a yellow film of oxide. Pure water does not act on it, except at a white heat; in water containing carbonic acid it forms a crystalline subcarbonate. Chlorine, bromine, and iodine combine with it directly. Hot sulphuric acid dissolves it as sulphate. Nitric acid dissolves it as nitrate.

It is usually contaminated with arsenic, from which it is best purified by heating to redness a mixture of powdered bismuth, potassium carbonate, soap, and charcoal, under a layer of charcoal. After an hour the mass is cooled; the button is separated and fused until its surface begins to be coated with a yellowish brown oxide.

Oxides.—Four oxides are known: Bi_2O_2, Bi_2O_3, Bi_2O_4, Bi_2O_5.

Bismuth Trioxide—*Protoxide—Bismuthi oxidum* (Br.)—Bi_2O_3—is formed by decomposing a bismuth or bismuthyl salt by an alkali, and boiling the liquid on the precipitate. It is a pale yellow, insoluble powder; sp. gr. 8.2; fuses at a red heat. It is reduced by hydrogen or charcoal. It dissolves in hydrochloric and nitric acids, and in fused potash.

Hydrates.—Bismuth forms at least four hydrates: *Bismuthous hydrate*, $Bi'''H_3O_3$, is formed as a white precipitate when potash or ammonia is added to a cold solution of a bismuth salt. This hydrate, when dried, loses water and forms bismuthyl hydrate $(BiO)'HO$. *Bismuthic acid*, $(BiO_3)'HO$, is deposited as a red powder when chlorine is passed through a boiling solution of potash holding bismuthous hydrate in suspension. *Pyrobismuthic acid*, $Bi_2O_7H_4$, is a dark brown powder, precipitated from solutions of bismuth nitrate by potassium cyanide.

Salts of bismuth.—Nitrate, $(NO_3)_3Bi$—obtained by dissolving bismuth in nitric acid and crystallizing. It crystallizes with 5 Aq. in large, colorless prisms; at 150°, or on contact with water, it is converted into bismuthyl nitrate; at 260°, into the trioxide.

Salts of bismuthyl.—They contain the group $(BiO)'$, and are formed from the corresponding bismuth salt by the action of water.

Nitrate—*Subnitrate* or *Magistery of bismuth—Bismuthi subnitras* (U. S., Br.)—$NO_3(BiO)$—is formed by decomposing a solution of bismuth nitrate with a large quantity of water. In its preparation for use in medicine, measures must be taken to separate arsenic; in the Br. P. process, the bismuth itself is purified; in the U. S. P. method, bismuth nitrate is decomposed by sodium carbonate; the bismuthyl nitrate so formed is washed, redissolved in nitric acid, the solution slowly precipi-

tated with ammonium hydrate, and the product washed. In the latter process it is expected that the arsenic will be washed out as sodium arsenate, an end seldom attained in practice.

It is a heavy, white powder, faintly acid; when recently precipitated, water dissolves it in small quantity, but deposits it again on standing. It is decomposed by pure water, but not by water containing $\frac{1}{500}$ ammonium nitrate. It usually contains 1 Aq., which it loses at 100°.

The cosmetic known as *pearl white* is sometimes this salt, sometimes bismuthyl chloride.

CARBONATE—*Bismuthi subcarbonas* (U. S.)—*Bismuthi carbonas* (Br.) —$CO_3(BiO)_3$—a white precipitate, formed by alkaline carbonates in solutions of bismuth nitrate. Heat decomposes it into carbon dioxide and bismuth trioxide.

Analytical characters. — *Water*, white precipitate, even in the presence of tartaric acid, but not in presence of nitric, hydrochloric, or sulphuric acid. *Hydrogen sulphide*, black precipitate, insoluble in dilute acids and in alkaline sulphides. *Ammonium sulphydrate*, black precipitate, insoluble in excess. *Potash, soda*, or *ammonium hydrate*, white precipitate, insoluble in excess and in tartaric acid, turns yellow when the liquid is boiled. *Potassium ferrocyanide*, white precipitate, insoluble in hydrochloric acid. *Potassium ferricyanide*, yellowish precipitate, soluble in hydrochloric acid. *Infusion of galls*, orange precipitate. *Potassium iodide*, brown precipitate, soluble in excess.

Action on the economy.—Although the medicinal compounds of bismuth probably are poisonous, if taken in sufficient quantity, the ill effects ascribed to them are in most, if not all cases, referable to contamination with arsenic. Symptoms of arsenical poisoning have not only been frequently observed when the subnitrate has been taken internally, but also when it has been used as a cosmetic.

When preparations of bismuth are administered, the alvine discharges contain bismuth sulphide as a dark brown powder.

VII. TIN GROUP.

TITANIUM, Ti., 50; TIN, Sn., 118; ZIRCONIUM, Zr., 89.6.

Titanium and tin are divalent in one series of compounds, $SnCl_2$, and quadrivalent in another, $SnCl_4$. Zirconium, so far as known, is always quadrivalent. Each of these elements forms an acid (or salts corresponding to one) of the composition MO_3H_2, and a series of oxysalts of the composition $(NO_3)_4M^{IV}$.

TIN.

Stannum.....Sn.....118

The only member of this group of practical interest, is obtained chiefly from a native stannic oxide, *cassiterite* or *tinstone*.

When required pure, commercial tin is dissolved in hydrochloric acid, the solution filtered and evaporated; the chloride dissolved in water and decomposed with ammonium carbonate; the protoxide reduced by charcoal.

Tin is a bluish white metal, soft, malleable, ductile; sp. gr. 7.285 when cast, 7.293 when hammered; fuses at 228°; emits a peculiar sound, the *tin cry*, when bent.

Air affects it but little at ordinary temperatures; when heated in air it is oxidized; more rapidly if alloyed with lead. It oxidizes slowly in water, more rapidly in salt water; if alloyed with lead, that metal is more readily dissolved by water than when it is pure. Hydrochloric acid dissolves it as stannous chloride. Nitric acid, in presence of a small quantity of water, converts it into metastannic acid. Alkaline solutions dissolve it as metastannates. Chlorine, bromine, iodine, sulphur, phosphorus, and arsenic combine with it directly.

It is used in the arts principally to protect iron or copper surfaces from atmospheric influences. *Tin plates* are thin sheets of iron coated with tin. Copper and iron vessels are *tinned*, after brightening, by contact with molten tin. The practice of using an alloy of lead and tin in tinning is to be avoided, as the lead, when thus alloyed, is readily dissolved. *Tin-foil*, thin laminæ of tin, is used to exclude air and moisture, and in the silvering of mirrors. Pewter, bronze, bell metal, speculum metal, gun metal, britannia metal, solder and Rose's alloy, contain tin. The compounds of tin are largely used in dyeing.

Oxides.—Two oxides are known, SnO and SnO_2.

Stannic Oxide—*Binoxide of tin*—SnO_2—exists in nature as *cassiterite*, and is formed when tin or stannous oxide is calcined in air. Under the name *putty powder* it is used as a polishing material.

Hydrates.—*Stannous hydrate*, SnH_2O_2—is a white precipitate produced by alkaline hydrates and carbonates in a solution of stannous chloride. *Stannic acid*, SnO_2H_2, is formed by the action of the same reagents on stannic chloride. *Metastannic acid*, $Sn_5O_{11}H_2$, is a white, insoluble powder, formed by acting on tin with concentrated nitric acid.

Chlorides.—Two chlorides of tin are known:

Stannous Chloride—*Protochloride of tin—Tin crystals*—$SnCl_2$—is obtained by dissolving tin in hydrochloric acid. It crystallizes with 2 Aq. in colorless prisms, soluble in a small quantity of water, but decomposed, with formation of an oxychloride, by a large quantity, unless hydrochloric acid be added. In air it is converted into stannic chloride and oxychloride. Oxidizing and chlorinating agents convert it into stannic chloride. It is a useful reducing agent, separates gold from its chloride, and converts mercuric chloride into mercurous chloride and mercury. It is used as a mordant in dyeing.

Stannic Chloride—*Bichloride of tin—Liquid of Libavius*—$SnCl_4$—is formed from the preceding compound, or by the action of dry chlorine on tin, as a fuming, yellowish liquid; sp. gr. 2.28; boils at 120°.

Salts.—Stannous Nitrate, $(NO_3)_2Sn$—formed when stannous hydrate is dissolved in nitric acid. The solution deposits metastannic acid.

Stannic Nitrate, $(NO_3)_4Sn$—formed when stannic oxide is dissolved in nitric acid.

Stannous Sulphate, SO_4Sn, and Stannic Sulphate, $(SO_4)_2Sn$—are produced, the former when stannous hydrate is dissolved in hot dilute sulphuric acid, and the latter when tin is dissolved in strong boiling sulphuric acid.

Analytical characters.—Stannous.—*Potash* or *Soda*, white precipitate, soluble in excess; the solution deposits tin when boiled. *Ammonium hydrate*, white precipitate, insoluble in excess; turns olive-brown when the liquid is boiled. *Hydrogen sulphide*, dark brown precipitate,

soluble in potash, alkaline sulphides, and hot hydrochloric acid. *Mercuric chloride*, white precipitate, turning gray and black. *Auric chloride*, purple or brown precipitate in presence of a small quantity of nitric acid. *Zinc*, deposit of tin.

STANNIC.—*Potash* or *Ammonium hydrate*, white precipitate, soluble in excess. *Hydrogen sulphide*, yellow precipitate, soluble in alkalies, alkaline sulphides, and hot hydrochloric acid. *Sodium hyposulphite*, yellow precipitate, when heated.

VIII. PLATINUM GROUP.

PALLADIUM, Pd., 106.5; PLATINUM, Pt., 198.

IX. RHODIUM GROUP.

RHODIUM, Rh., 104; RUTHENIUM, Ru., 104; IRIDIUM, Ir., 197.2.

The elements of these two groups, together with osmium, are usually classed as "metals of the platinum ores." They all form hydrates (or salts representing them) having acid properties. Osmium has been removed because the relations existing between its compounds and those of molybdenum and tungsten are much closer than those which they exhibit to the compounds of these groups. The separation of the remaining platinum metals into two groups is based upon resemblances in the composition of their compounds, as shown in the following table:

Chlorides.				*Oxides.*			
$PdCl_2$	$PtCl_2$	$RhCl_2$	$RuCl_2$ ..?	PdO	PtO	RhO	RuO ..IrO
$PdCl_4$	$PtCl_4$	——	$RuCl_4$ ..$IrCl_4$ ..	——	——	Rh_2O_3	Ru_2O_3..Ir_2O_3
——	——	Rh_2Cl_6	Ru_2Cl_6..Ir_2Cl_6..	PdO_2	PtO_2	RhO_2	RuO_2 ..IrO_2
				——	——	RhO_3	RuO_3 ..IrO_3
				——	——	——	RuO_4 ..——

PLATINUM.

Pt 198

Exists in nature, associated with the other platinum metals, gold, lead, and iron; the ores containing 45 to 86 per cent. of platinum.

It is a grayish white metal, sp. gr. 21.1 when cast, 21.5 when hammered; softens at a white heat; may be welded; fuses with difficulty; very malleable, ductile, and tenacious. When obtained by heating the double chloride of platinum and ammonium it forms a grayish mass, called *spongy platinum*. It is not oxidized by air or oxygen; combines directly with chlorine, phosphorus, arsenic, silicon, sulphur, and carbon. Aqua regia is the only acid which dissolves it. Platinum vessels are perforated or deteriorated when heated with metals, easily reducible metallic oxides, mixtures capable of liberating chlorine, and phosphates, silicates, hydrates, nitrates, or carbonates of the alkaline metals.

Platinic chloride, $PtCl_4$—formed by dissolving platinum in aqua regia. It crystallizes in very soluble, yellow needles, whose solution is valuable as a test for ammonium and potassium.

CLASS IV.

ELEMENTS WHOSE OXIDES UNITE WITH WATER TO FORM BASES; NEVER TO FORM ACIDS. WHICH FORM OXYSALTS.

I. SODIUM GROUP.

Alkaline Metals.

LITHIUM	Li 7	RUBIDIUM	Rb 85.4
SODIUM	Na 23	CÆSIUM	Cs 132.6
POTASSIUM	K 39	SILVER	Ag ..... 108.

Each of the elements of this group forms a single chloride, M'Cl, and one or more oxides, the most stable of which has the composition M'_2O; they are, therefor, univalent. Their hydrates, M'HO, are more or less alkaline and have markedly basic characters. Silver resembles the other members of the group in chemical properties, although it does not in physical characters.

LITHIUM.

Li.....7

A silver-white metal; tarnishes rapidly in air; is the lightest of the solid elements; sp. gr. 0.589; fuses at 180°; burns in air; decomposes water at the ordinary temperature.

Oxide, Li_2O—is a white solid, formed by burning lithium in dry oxygen. It dissolves slowly in water with formation of the *hydrate*, LiHO.

Chloride, LiCl—crystallizes in regular octahedra; very deliquescent; forms a double chloride with platinic chloride, which is soluble in water and in alcohol.

Bromide — *Lithii bromidum*—LiBr—is formed by decomposing lithium sulphate with potassium bromide. Also by saturating a solution of hydrobromic acid with lithium carbonate. It forms deliquescent needles, which contain 91.95 per cent. of bromine.

Salts.—CARBONATE—*Lithii carbonas* (U. S.)—CO_3Li_2—obtained by fusing *lepidolite*, a native silicate, with barium sulphate and carbonate and potassium sulphate; extracting with water, and precipitating with sodium carbonate. The product is purified by repeated washing with water, suspension in water through which carbon dioxide is passed, and reprecipitation by boiling the solution. It is soluble in water to the extent of 1.2 parts per 100; 5.25 parts per 100 in water containing carbonic acid; insoluble in alcohol. With uric acid it forms lithium urate (*q. v.*).

Analytical characters.—*Ammonium carbonate*, white precipitate in concentrated solutions, never in dilute solutions or in presence of large quantities of ammoniacal salts. *Sodium phosphates*, white precipitate

in neutral or alkaline solution, soluble in acids and in solutions of ammoniacal salts. It colors the Bunsen flame bright red, and has a spectrum of two bright lines—λ=6705 and 6102.

SODIUM.

Natrium.....Na.....23.043

Sodium is now obtained by a process based upon the reduction of the carbonate by coal. A mixture of dry sodium carbonate, coal, and chalk is heated to whiteness in iron retorts, connected with suitable recipients, in which the distilled metal is collected under a layer of naphtha.

It is a silver-white metal, is rapidly tarnished in air, and becomes coated with a brownish yellow layer. At ordinary temperatures it is of waxy consistency; at 95.6° it fuses; at a white heat it volatilizes; sp. gr. 0.972 at 15°.

In air it is gradually oxidized from the surface inward, but may be kept in well-closed vessels without the protection of a layer of naphtha. It decomposes water; frequently, if the sodium have been long kept, with an explosion. It burns with a yellow flame. Its affinities are the same as, but less active than, those of potassium.

Oxides.—Three oxides of sodium have been described, Na_4O, Na_2O, Na_2O_2. The *protoxide*, Na_2O, is a grayish white mass, formed when sodium is burned in dry air, or by action of sodium upon sodium hydrate.

Hydrate—*Caustic soda*—*Soda* (U. S., Br.)—NaHO—is formed when water is decomposed by sodium. It is usually obtained by decomposing the carbonate with caustic lime or baryta. The solution is decanted from the earthy carbonate and evaporated in a silver basin, in which the residue is fused and cast into cylindrical moulds. It is purified by solution in alcohol and evaporation. The *soda by baryta* is purer than the *soda by lime;* the latter frequently contains arsenic.

It is opaque, white, fibrous, brittle, fusible below redness, sp. gr. 2.00; very soluble in water; its solutions, known in the arts as *Soda lye*, and in pharmacy as *Liq. sodæ* (the latter of sp. gr. 1.071), are intensely caustic and alkaline. When exposed to air it absorbs water and is converted into the carbonate.

Soda solutions attack glass very readily; the necks and stoppers of bottles containing them should be well coated with paraffine.

Chloride—*Common salt*—*Sea salt*—*Table salt*—*Sodii chloridum* (U. S., Br.)—NaCl—occurs abundantly in nature, deposited in the solid form as rock salt, in solution in all natural waters, in suspension in the atmosphere, and as a constituent of almost all vegetable and animal tissues. It is formed in an infinite variety of chemical reactions. It is obtained from the natural deposits of rock salt; or by evaporation of sea-water or the water of saline springs. It is the source from which all the compounds of sodium are industrially obtained, directly or indirectly.

It crystallizes in anhydrous cubes or octahedra; sp. gr. 2.078; fuses at a red heat, and crystallizes on cooling; at a white heat it volatilizes sensibly. One part of the salt dissolves in 2.78 parts of water at 14°; in 2.7 parts at 60°, and in 2.48 parts at 109.7°. Dilute solutions, on freezing, yield pure ice. Hydrochloric acid precipitates it from its concentrated solution. It is insoluble in absolute alcohol, sparingly soluble

in weak alcohol. Sulphuric acid decomposes it with formation of sodium sulphate and liberation of hydrochloric acid.

Physiological.—Sodium chloride exists in every animal tissue and fluid, and is present in the latter, especially the blood, in tolerably constant proportion. It is introduced with the food, either as a constituent of the alimentary substances, or as a condiment. In the body it serves to aid the phenomena of osmosis and to maintain the solution of the albuminoids. It is probable, also, that it is decomposed in the gastric mucous membrane with formation of free hydrochloric acid.

It is discharged from the economy by all the channels of elimination, notably by the urine, when the supply by the food is maintained. If, however, the food contain no salt, it disappears from the urine before it is exhausted from the blood.

The amount of chlorine (mainly in the form of sodium chloride) voided by a normal male adult in 24 hours is about 10 grams, corresponding to 16.5 grams of sodium chloride. When normal or excessive doses are taken, the amount eliminated by the urine is less than that taken in; when small quantities are taken, the elimination is at first in excess of the supply. The hourly elimination increases up to the seventh hour, when it again diminishes. The amount of sodium chloride passed in the urine is less than the normal in acute, febrile diseases; in intermittent fever it is diminished during the paroxysms, but not during the intervals. In diabetes it is much increased, sometimes to 29 grams per diem.

Quantitative determination of chlorides in urine.—The process is based upon the formation of the insoluble silver chloride, and upon the formation of the brown silver chromate in neutral liquids, in the absence of soluble chlorides. The solutions required are:

First.—A solution of silver nitrate of known strength, made by dissolving 29.075 grams of pure, fused silver nitrate (see p. 407) in a litre of water. *Second.—A solution of neutral potassium chromate.*

To conduct the determination, 5—10 c.c. of the urine are placed in a platinum basin, 2 grams of sodium nitrate (free from chloride) are added; the whole is evaporated to dryness over the water-bath, and the residue heated gradually until a colorless, fused mass remains. This, on cooling, is dissolved in water, the solution placed in a small beaker, treated with pure, dilute nitric acid to faintly acid reaction, and neutralized with calcium carbonate. Two or three drops of the chromate solution are added, and then the silver solution from a burette, during constant stirring of the liquid in the beaker, until a faint reddish tinge remains permanent. Each c.c. of the silver solution used represents 10 milligrams of sodium choride (or 6.065 milligrams of chlorine) in the amount of urine used.

Example.—5 c.c. urine used, 6 c.c. silver solution added; 1,200 c.c. urine passed in 24 hours: $\therefore \frac{0.01+6}{5} \times 1{,}200 = 14.4$ grams NaCl in 24 hours.

If the urine contain iodides or bromides, they must be removed by acidulating the solution of the residue of incineration with sulphuric acid, removing the iodine or bromine by shaking with carbon disulphide, neutralizing the aqueous solution with calcium carbonate and proceeding as above.

Bromide, NaBr.—formed by dissolving bromine in a solution of caustic soda to saturation, evaporating to dryness, calcining the residue at a dull red heat; redissolving in water, filtering and crystallizing. It crystallizes in anhydrous cubes; soluble in 1.13 parts of water at 20°,

and in 0.87 at 100°; soluble in alcohol. It contains 77.67 per cent. of bromine.

Iodide, NaI—prepared by heating together water, iron-filings, and iodine in fine powder, filtering, adding an equivalent quantity of sodium sulphate and some slacked lime; boiling, decanting, and evaporating. It crystallizes in anhydrous cubes; soluble in 0.56 parts of water at 20°, and in 0.32 at 100°; soluble in alcohol. It contains 84.66 per cent. of iodine.

Salts of Sodium.—NITRATE—*Cubic saltpetre—Chili saltpetre—Sodii nitras* (U. S.)—NO_3Na—occurs in natural deposits in Chili and Peru. It crystallizes in anhydrous rhombohedra; is deliquescent; has a cooling, saline, and somewhat bitter taste; fuses at 310°, and, when strongly heated, is decomposed with formation of nitrite, and then of hydrate of sodium and nitric acid; very soluble in water; less soluble in water containing free nitric acid; sparingly soluble in alcohol.

It is used in the manufacture of saltpetre, in the manufacture of nitric acid, sodium sulphate being a byproduct, and as a fertilizer.

Sulphates.—There are five sodium sulphates: SO_4NaH, SO_4Na_2, $S_2O_7Na_2$, $(SO_4)_2Na_3H$, and $(SO_4)_2NaH_3$.

Hydrosodic sulphate—Acid sodium sulphate—Sodium bisulphate—SO_4NaH—crystallizes in long, four-sided prisms; is unstable, and is decomposed by exposure to air, by water or by alcohol, into sulphuric acid and the neutral sulphate. When heated to dull redness, it is converted into the *pyrosulphate*, $S_2O_7Na_2$, corresponding to pyrosulphuric or Nordhausen acid.

Sodic sulphate—Neutral sodium sulphate—Glauber's salt—Sodii sulphas (U. S.)—*Sodæ sulphas* (Br.)—SO_4Na_2—occurs in nature in the solid form, and in solution in many natural waters. It is obtained as a step in the manufacture of the carbonate (*q. v.*), from the natural deposits, from the mother-liquors of the preparation of sodium chloride, and as a byproduct in the manufacture of nitric acid; principally by the decomposition of sodium chloride by sulphuric acid.

It crystallizes with water in two proportions, 7 Aq. and 10 Aq. The salt, $SO_4Na_2+7Aq.$ is deposited from saturated or supersaturated solutions at +5°. The salt, SO_4Na_2+10 Aq. is that usually met with and which is used in pharmacy. It crystallizes in large, colorless, oblique, rhombic prisms, which effloresce in air and gradually lose all their Aq. It fuses at 33° in its water of crystallization, and is gradually converted into the anhydrous salt. If fused at 33° and allowed to cool, it remains liquid in *supersaturated* solution, from which it is deposited, the entire mass becoming crystalline on contact with the smallest particle of foreign matter. It is sparingly soluble in alcohol.

Physiological.—The neutral sulphates of sodium and potassium seem to exist in small quantity in all animal tissues and fluids, with the exception of milk, bile, and gastric juice; they certainly exist in the blood and urine. They are partially introduced with the food, and in part formed in the body as a result of the metamorphosis of those constituents of the tissues which contain sulphur in organic combination.

The principal elimination of the sulphates is by the urine. All the sulphuric acid in the urine is not in simple combination with the alkaline metals, a considerable amount exists in the form of the alkaline salts of conjugate, monobasic ether acids, which on decomposition yield an aromatic organic compound. The amount of sulphuric acid discharged by the urine in twenty-four hours, in the form of alkaline sulphates, is

from 2.5 to 3.5 grams; that eliminated in the salts of the conjugate acids, 0.617 to 0.094 gram.

HYPOSULPHITE—*Sodii hyposulphis* (U. S.)—$S_2O_3Na_2+5Aq.$—is obtained by fusing together sulphur and sodium carbonate; oxidizing the sulphide so formed; dissolving sulphur in the hot, concentrated solution of the sulphite, and crystallizing.

It crystallizes in large, colorless prisms, which fuse at 45°. One part dissolves in 1.44 part of water at 20°; and in 0.52 part at 60°. It is insoluble in alcohol. Its solutions precipitate alumina from its salts without precipitating iron or manganese; they dissolve many compounds which are insoluble in water; cuprous hydrate, iodides of lead, silver, and mercury, lead and calcium sulphates. It acts as a disinfectant, and is preservative of animal tissues.

SILICATES.—If silex and sodium carbonate be fused together, the residue extracted with water and the solution evaporated, a transparent, glass-like mass, soluble in hot water, remains; this is *soluble glass* or *water-glass*. When exposed to the air in contact with stone, it becomes entirely insoluble, and is used to render stone structures impermeable.

PHOSPHATES.—Three salts derived from orthophosphoric acid exist:

Trisodic phosphate—Basic sodium phosphate—$PO_4Na_3+12Aq.$—is obtained by adding sodium hydrate to disodic phosphate and evaporating to crystallization. It crystallizes in six-sided prisms; soluble in 5.1 parts of water at 15.5°. The solution is alkaline in reaction, and by exposure to air absorbs carbon dioxide with formation of disodic phosphate, and sodium carbonate.

Disodic phosphate—Hydrodisodic phosphate—Neutral sodium phosphate — Phosphate of soda — Sodii phosphas (U. S.) — *Sodæ phosphas* (Br.)—$PO_4Na_2H+12Aq.$—is obtained by converting tricalcic phosphate (bone phosphate) into monocalcic phosphate, and decomposing that salt with sodium carbonate. It crystallizes below 30° in oblique, rhombic prisms with 12 Aq.; at 33°, it crystallizes with 7 Aq. The salt with 12 Aq. effloresces in air and readily parts with 5 Aq.; it is soluble in four parts of cold water and in two parts of boiling water; that with 7 Aq. is not efflorescent and dissolves in eight parts of water at 23°. Its solutions are faintly alkaline. It is insoluble in alcohol.

Monosodic phosphate—Acid sodium phosphate — $PO_4NaH_2+Aq.$—crystallizes in rhombic prisms. At 100° it loses its Aq., and, at about 200° is converted into an *acid pyrophosphate*, $P_2O_7Na_2H_2$, which at 204° is converted into the *metaphosphate*, PO_3Na. It is very soluble in water and insoluble in alcohol. Its solutions are acid in reaction.

Physiological.—All the sodium phosphates exist, accompanied by the corresponding potassium salts, in the animal economy. The disodic and dipotassic phosphates are the most abundant, and of these two the former. They exist in every tissue and fluid of the body, and are more abundant in the fluids of the carnivora than in those of the herbivora. In the blood, in which the sodium salt predominates in the plasma, and the potassium salt in the corpuscles, they serve to maintain an alkaline reaction. With strictly vegetable diet the proportion of phosphates in the blood diminishes, and that of the carbonates (the predominating salts in the blood of the herbivora) increases.

The monosodic and monopotassic phosphates exist in the urine, the former predominating, and to their presence the acid reaction of that fluid is largely due. They are produced by decomposition of the neutral

salts by uric acid. The urine of the herbivora, whose blood is poor in phosphates, is alkaline in reaction.

The greater part of the phosphates in the body are introduced with the food; a portion is formed in the economy by the oxidation of phosphorized organic substances, the lecithins. (See p. 286).

Borates.—Six sodium borates have been described; the only one requiring mention is *Disodic tetraborate; Sodium pyroborate; Borate of sodium; Borax; Tincal; Sodii boras* (U. S.)—$Bo_4O_7Na_2+10Aq.$—is now prepared chiefly from the boracic acid of Tuscany, which is boiled with a proper quantity of sodium carbonate and crystallized. It crystallizes in hexagonal prisms with 10 Aq., or in regular octahedra with 5 Aq. The former variety is permanent in moist air, but effloresces in dry air, and is soluble in 12 parts of cold and in 2 parts of boiling water; the latter is permanent in dry air. Either form, when heated, fuses in its Aq., and swells considerably; at a red heat it becomes anhydrous, and on cooling forms a clear, glassy mass.

It is fatal to the lower forms of animal life, and is a safe and efficient agent for driving off insect vermin.

Hypochlorite, ClONa—is obtained in solution in the *Liq. sodæ chlorinatæ* (U. S.); *Liq. sodæ chloratæ* (Br.); or *Labarraque's solution*, by decomposing a solution of chloride of lime (*q. v.*) with sodium carbonate and filtering. It is readily decomposed, giving up a portion of its chlorine, which, being in the nascent state, acts as an efficient decolorizing and disinfecting agent.

Permanganate, MnO_4Na—is prepared in the same way as the potassium salt (*q. v.*), which it resembles in its properties. It enters into the composition of *Condy's fluid*, and of the disinfectant known as *chlorozone*, which is a solution of sodium permanganate and hypochlorite.

Acetate—*Sodii acetas* (U. S.)—*Sodæ acetas* (Br.)—$C_2H_3O_2Na+3Aq.$—is prepared by distilling purified calcium pyrolignite with sulphuric acid, neutralizing with sodium carbonate, and crystallizing. It crystallizes in large, colorless prisms; has a sharp, bitterish taste; is soluble in 3.9 parts of water at 6°; soluble in alcohol; in dry air it loses 3 Aq., which it takes up again from moist air. Heated with soda-lime, it is decomposed with production of marsh-gas. The anhydrous salt, heated with sulphuric acid, yields glacial acetic acid.

Carbonates.—Three sodium carbonates are known: CO_3Na_2, CO_3NaH, $(CO_3)_3Na_4H_2$. *Sodium carbonate—Neutral carbonate of soda—Soda—Sal soda—Washing soda—Soda crystals—Sodii carbonas* (U. S.)—*Sodæ carbonas* (Br.)—CO_3Na_2—is industrially the most important of the sodium compounds, and is manufactured in enormous quantity from the chloride by Leblanc's or Solvay's processes; or from *cryolite*, a native fluoride of sodium and aluminium.

Leblanc's process, in its present form, consists of three distinct processes: *First.*—The conversion of sodium chloride into the sulphate by decomposition by sulphuric acid. *Second.*—The conversion of the sulphate into carbonate by heating a mixture of the sulphate with calcium carbonate and charcoal. The product of this reaction, known as *black ball soda*, is a mixture of sodium carbonate with charcoal and calcium sulphide and oxide. *Third.*—The purification of the product obtained in Second. The ball black is broken up, disintegrated by steam, and lixiviated. The solution, on evaporation, yields the *soda salt* or *soda* of commerce.

Of late years Leblanc's process has been in great part replaced by

Solvay's method, or ammonia process, which is more economical and yields a purer product. In this process sodium chloride and ammonium bicarbonate react upon each other with production of the sparingly soluble sodium bicarbonate and the very soluble ammonium chloride. The sodium bicarbonate is then simply collected, dried, and heated, when it is decomposed into carbonate, water, and carbon dioxide.

The anhydrous carbonate, *Sodii carbonas exsiccata* (U. S.), CO_3Na_2, is formed as a white powder by calcining the crystals. It fuses at dull redness and gives off a little carbon dioxide. It combines with and dissolves in water with elevation of temperature.

The crystalline sodium carbonate, $CO_3Na_2+10Aq.$, forms large rhombic crystals, which effloresce rapidly in dry air; fuse in their Aq. at 34°; are soluble in water, most abundantly at 38°, at which temperature 100 parts of water contain 51.67 parts of CO_3Na_2. The solutions are alkaline in reaction.

Hydrosodic carbonate—Monosodic carbonate—Bicarbonate of soda—Acid carbonate of soda—Vichy salt—Sodii bicarbonas—(U. S.)—*Sodæ bicarbonas* (Br.)—CO_3NaH—exists in solution in many mineral waters. It is obtained by the action of carbon dioxide upon the disodic salt in the presence of water.

It crystallizes in rectangular prisms, anhydrous and permanent in dry air; in damp air it gives off carbon dioxide and is converted into the sesquicarbonate, $(CO_3)_2Na_4H_2$. When heated it gives off carbon dioxide and water, and leaves the disodic carbonate; 100 parts of water dissolve 8.15 parts at 10°, and 16.4 parts at 60°; above 70° the solution gives off carbon dioxide. The solutions are alkaline.

Physiological.—The fact that the carbonates of sodium and potassium are almost invariably found in the ash of animal tissues and fluids, is no evidence of their existence there in life, as the carbonates are produced by the incineration of the sodium and potassium salts of organic acids. There is, however, excellent indirect proof of the existence of the alkaline carbonates in the blood, especially of the herbivora, in the urine of the herbivora at all times, and in that of the carnivora and omnivora when food rich in the salts of the organic acids, with alkaline metals, is taken. The carbonates in the blood are both the mono- and disodic and potassic; and the carbonic acid in the plasma is held partially in simple solution, and partly in combination in the monometallic carbonates.

Analytical Characters.—*Hydrofluosilicic acid*—a gelatinous precipitate, if not too dilute. *Potassium pyroantimoniate*, in neutral solution and in the absence of metals other than potassium and lithium, a white, flocculent precipitate, becoming crystalline on standing. *Periodic acid* in excess, a white precipitate if the solution be not too dilute. The Bunsen flame is colored yellow, and shows a brilliant double line occupying the position of the D-line of the solar spectrum; $\lambda=5895$ and 5889.

POTASSIUM.

Kalium .....K.....39.137

Is prepared by the same process as that used for obtaining sodium. It is a silver-white metal, brittle at 0°; waxy at 15°; at 62.5° it fuses; at a red heat it distils in green vapors, which condense in cubic crystals; sp. gr. 0.865 at 15°.

Potassium is the only metal which oxidizes at low temperatures in dry air, in which it is rapidly coated with a white layer of the hydrate, and frequently ignites, burning with a violet flame. It must be kept under naphtha. It decomposes water or ice with great energy, the reaction liberating heat enough to ignite the hydrogen which is set free. It combines with chlorine with incandescence, and also unites directly with sulphur, phosphorus, arsenic, antimony, and tin.

Oxides.—Two oxides of potassium are known, K_2O and K_2O_4.

Hydrate—*Potash*—*Potassa*—*Common caustic*—*Potassa* (U. S.)—*Potassa caustica* (Br.)—KHO—is obtained from potassium carbonate by decomposition with calcic hydrate. The solution is evaporated and the residue fused and cast into cylindrical moulds; the product is *potash by lime*. To purify it, it is dissolved in alcohol, the solution evaporated, the residue fused in a silver basin and cast in a silver mould; the product is *potash by alcohol*, and is free from potassium chloride and sulphate, but contains small quantities of the carbonate, and frequently arsenic.

It is usually met with in cylindrical sticks, hard, white, opaque, and brittle. The potash by alcohol has a bluish tinge, and a smoother surface than the common; sp. gr. 2.1; it fuses at dull redness; is freely soluble in water; less so in alcohol. The solutions have a soapy taste, and an alkaline reaction, and are strongly caustic. In air, it absorbs water and carbon dioxide, and is finally converted into the carbonate. Its solutions dissolve chlorine, bromine, iodine, sulphur, and phosphorus. It decomposes the ammoniacal salts with liberation of ammonia; and the salts of many of the metals with formation of a potassium salt and a hydrate of the metal. It dissolves the albuminoids with formation of an alkali albuminate; when heated with them, they are decomposed with formation of leucin, tyrosin, etc. It oxidizes the carbohydrates with formation of potassium carbonate and oxalate.

Sulphides.—Five sulphides, K_2S, K_2S_2, K_2S_3, K_2S_4, and K_2S_5, and a sulphydrate, KHS, are known. The *pentasulphide*, K_2S_5, is formed when excess of sulphur and potassium carbonate are fused together; the product is a brown mass, known as *liver of sulphur*, or *Potassii sulphuretum* (U. S.); *Potassa sulphurata* (Br.). It is readily decomposed, and on contact with hydrochloric acid gives off hydrogen sulphide.

Chloride—*Sal digestivum Sylvii*—KCl—exists in nature, either pure or mixed with other chlorides; at Stassfurth, a double chloride of potassium and magnesium, KCl, $MgCl_2+6Aq.$, called *carnallite*, is worked as a source of potassium compounds.

It crystallizes in anhydrous cubes; permanent in air; 100 parts of water dissolve 29.23 parts at 0°, and 0.2738 part more for every degree of elevation of temperature.

Bromide—*Potassii bromidum* (U. S., Br.)—KBr—is formed either by decomposing ferrous bromide by potassium carbonate, or by dissolving bromine in solution of potassium hydrate. In the latter case, a mixture of bromide and bromate is obtained, and the latter is converted into bromide by calcining the product.

It crystallizes in anhydrous cubes or tables; has a sharp, salty taste; is very soluble in water, sparingly so in alcohol. Chlorine decomposes it with liberation of bromine. It contains 67.22 per cent. of bromine.

Iodide—*Potassii iodidum* (U. S., Br.)—KI—is obtained by saturating potash solution with iodine, evaporating, and calcining the resulting mixture of iodide and iodate with charcoal. The product is very liable to contain iodate and carbonate.

It crystallizes in cubes, which are transparent if the iodide be pure; permanent in air, salty in taste; soluble to the extent of 100 parts, in 73.5 parts of water at 12.5°, and in 45 parts at 120°. It dissolves in 5.5 parts of alcohol of sp. gr. 0.85 at 12.5°. Chlorine and nitrous and nitric acids decompose it with liberation of iodine. It combines with many other iodides to form double iodides.

Salts.—NITRATE—*Nitre—Saltpetre—Potassii nitras* (U. S.)—*Potassæ nitras* (Br.)—NO_3K—exists naturally, and is formed artificially as a result of the decomposition of nitrogenized organic substances. The more usual process for its preparation is the decomposition of the native sodium nitrate, either by a boiling solution of potassium carbonate, or by potassium chloride.

It crystallizes in six-sided, rhombic prisms, which are grooved upon the surface. It dissolves in water with depression of temperature, and is more soluble in water containing sodium chloride; in alcohol it is very sparingly soluble. It fuses at 350°, without decomposition; at a temperature below redness it gives off oxygen, and is converted into the nitrite, NO_2K; when further heated it is decomposed into nitrogen, oxygen, and a mixture of the oxides. The readiness with which it gives up its oxygen, when heated in presence of an oxidizable substance, renders it valuable as an oxidizing agent.

Gunpowder is an intimate mixture of this salt with sulphur and carbon, in such proportion that the nitre contains all the oxygen required for the combustion.

CHLORATE—*Chlorate of potash—Potassii chloras* (U. S.)—*Potassæ chloras* (Br.)—ClO_3K—is prepared from potassium chloride; this is mixed with slaked lime, and the mixture, while heated to 60°, treated with chlorine until no further absorption of gas takes place, when it is drawn off, allowed to deposit, the clear solution rapidly evaporated, and the product purified by recrystallization.

It crystallizes in transparent, anhydrous plates. Soluble in water to the extent of 6.03 parts in 100 at 15.37°, and 24 parts at 104.7°; sparingly soluble in weak alcohol; fuses at 400°; if further heated, it is decomposed into chloride and perchlorate with liberation of oxygen, and at a still higher temperature the perchlorate is decomposed into chloride and oxygen.

It is a valuable source of oxygen, and a more active oxidizing agent than nitre. When mixed with readily oxidizable substances, carbon, sulphur, phosphorus, sugar, tannin, resins, etc., the mixtures explode when heated or subjected to shock, the violence of the explosion being such as to prevent the use of such mixtures as explosives. With strong sulphuric acid, potassium chlorate gives off peroxide of chlorine, Cl_2O_4, an explosive, yellowish gas. Nitric acid decomposes it with formation of nitrate and perchlorate, and liberation of chlorine and oxygen. Heated with hydrochloric acid, it gives a mixture of chlorine and peroxide of chlorine, the latter acting as an energetic oxidant in solutions in which it is generated.

HYPOCHLORITE, ClOK—is formed in solution by imperfect saturation of a cooled solution of potash with hypochlorous acid. An impure solution is used in bleaching, under the name of *Javelle water*.

SULPHATES.—Two sulphates, formed from single molecules of the acid, exist, SO_4K_2 and SO_4KH. Besides these, others are known, such as $(SO_4)_2K_4H_2$, $(SO_4)_2K_2H$, and the *pyrosulphate*, $S_2O_7K_2$.

Sulphate—Dipotassic sulphate—Potassii sulphas—(U. S.)—*Potassæ*

sulphas—(Br.)—SO_4K_2—exists in the Stassfurth mines, in the ash of many plants, and in solution in mineral waters. It is obtained from the Stassfurth deposits, and as an accessory product in many chemical manufacturing processes.

It crystallizes in right rhombic prisms; hard, permanent in air; salt and bitter in taste; soluble in water to the extent of 10.5 parts in 100 at 12°, and 26.3 parts at 101.5°.

Hydropotassic sulphate—Monopotassic sulphate—Acid sulphate—SO_4KH—is formed as a by-product in the manufacture of nitric acid. When heated it loses water, and is converted into the *pyrosulphate*, $S_2O_7K_2$, which, at a higher temperature, is decomposed into the dipotassic salt and sulphur trioxide.

SULPHITES.—Three sulphites, SO_3K_2, SO_3KH, and $S_2O_5K_2$, are known.

Sulphite—Dipotassic sulphite—Neutral potassium sulphite—Potassii sulphis (U. S.)—SO_3K_2—is formed by saturating a solution of the carbonate with sulphur dioxide, and evaporating over sulphuric acid. It crystallizes in oblique rhombic octahedra, which have a sulphurous odor and are very soluble in water. Its solution, when exposed to air, absorbs oxygen, and the salt is converted into the sulphate.

CHROMATE—*Neutral chromate*—CrO_4K_2—is formed by heating a mixture of *chrome iron ore*, $FeCr_2O_4$, and potassium nitrate or carbonate in contact with air; the residue is extracted with water; the solution neutralized with dilute sulphuric acid and evaporated. The dichromate thus formed is dissolved in water and converted into the chromate by neutralization with a suitable quantity of potassium carbonate.

DICHROMATE—*Bichromate—Potassii bichromas* (U. S.)—*Potassæ bichromas* (Br.)—$Cr_2O_7K_2$—is prepared as described above. It forms large, reddish orange colored, prismatic crystals; soluble in water; fuses below redness, and at a higher temperature is decomposed into oxygen, potassium chromate, and sesquioxide of chromium. Hydrochloric acid heated with it gives off chlorine.

PERMANGANATE—*Potassii permanganas* (U. S.)—*Potassæ permanganas* (Br.)—MnO_4K—is obtained by fusing a mixture of manganese dioxide, potash, and potassium chlorate, and evaporating the solution to crystallization; potassium manganate and chloride are first formed; on boiling with water the manganate is decomposed into potassium permanganate and hydrate, and manganese dioxide.

It crystallizes in dark prisms, almost black, with greenish reflections, which yield a red powder when broken. Soluble in water, communicating to it a red color, even in very dilute solution. It is a most valuable oxidizing agent; with organic matter its solution is turned to green by the formation of the manganate, or deposits the brown sesquioxide of manganese, according to the nature of the organic substance; in some instances the reaction takes place best in the cold, in others under the influence of heat; in some better in acid solutions, in others in alkaline solutions. Mineral reducing agents act more rapidly. Its oxidizing powers render its solutions valuable as disinfectants.

ACETATE—*Potassii acetas* (U. S.)—*Potassæ acetas* (Br.)—$C_2H_3O_2K$—exists in the sap of plants; and it is by its calcination that the major part of the carbonate of wood ashes is formed. It is prepared by neutralizing acetic acid with carbonate or bicarbonate of potassium.

It forms crystalline needles, deliquescent, and very soluble in water; less soluble in alcohol. Its solutions are faintly alkaline.

CARBONATES.—*Dipotassic carbonate—Salt of tartar—Pearlash—Po-*

tassii carbonas (U. S.)—*Potassæ carbonas* (Br.)—CO_3K_2—exists in mineral waters and in the animal economy. It is prepared industrially in an impure form, known as *potash* or *pearlash*, from wood ashes, from the molasses of beet-sugar, and from the native Stassfurth chloride. It is obtained pure by decomposing the monopotassic salt, purified by several recrystallizations, by heat; or by calcining a potassium salt of an organic acid. Thus cream of tartar mixed with nitre and heated to redness yields a black mixture of carbon and potassium carbonate, called *black flux;* on extracting which with water, a pure carbonate, known as *salt of tartar*, is left.

It occurs as a white, granular, deliquescent powder; quite soluble in water; insoluble in alcohol. Its solutions are strongly alkaline.

Hydropotassic carbonate—Monopotassic carbonate—Bicarbonate of potassium—Potassii bicarbonas (U. S.)—*Potassæ bicarbonas* (Br.)—CO_3KH—is obtained by dissolving the carbonate in water and saturating the solution with carbon dioxide. It crystallizes in oblique rhombic prisms, much less soluble than the carbonate. In solution it is gradually converted into the dipotassic salt when heated, when brought into a vacuum, or when treated with an inert gas. The solutions are alkaline in reaction and in taste, but are not caustic.

The substance used in baking, under the name *salæratus*, is this or the corresponding sodium salt. Its extensive use in some parts of the country is undoubtedly in great measure the cause of the prevalence of dyspepsia. When used alone in baking it "raises" the bread by decomposition into carbon dioxide and dipotassic (or disodic) carbonate, the latter producing disturbances of digestion by its strong alkaline reaction.

Oxalates.—Three oxalates are known: *Potassium oxalate—Neutral oxalate*—$C_2O_4K_2+Aq.$, is formed when oxalic acid is saturated with potassium carbonate. It forms rhombic prisms, very soluble in water, insoluble in alcohol. *Hydropotassic oxalate—Monopotassic oxalate—Binoxalate of potash*—C_2O_4KH. The *salt of sorrel*, or *salt of lemon*, is a mixture of this salt with the *quadroxalate*, $C_2O_4HK,C_2O_4H_2+2Aq$. It is used in straw-bleaching and for the removal of ink-stains. It closely resembles Epsom salt in appearance, and has been the cause of many cases of oxalic acid poisoning.

Tartrates.—*Potassic tartrate—Dipotassic tartrate—Soluble tartar—Neutral tartrate of potash—Potassii tartras* (U. S.)—*Potassæ tartras* (Br.)—$C_4H_4O_6K_2$—is prepared by neutralizing the hydropotassic salt with potassium carbonate. It forms a white, crystalline powder, very soluble in water, the solution being dextrogyrous, $[a]_D=+28.48°$; soluble in 240 parts of alcohol. Acids, even acetic, decompose its solution with precipitation of the monopotassic salt.

Hydropotassic tartrate—Monopotassic tartrate—Cream of tartar—Potassii bitartras (U. S.)—*Potassæ bitartras* (Br.)—$C_4H_4O_6HK$. During the fermentation of grape juice, as the proportion of alcohol increases, crystalline crusts collect in the cask. These constitute the *crude tartar* or *argol* of commerce, which is composed, in great part, of monopotassic tartrate. The crude product is purified by repeated crystallization from boiling water; digesting the purified tartar with hydrochloric acid at 20°; washing with cold water, and crystallizing from hot water.

It crystallizes in hard, opaque (translucent when pure), rhombic prisms, which have an acidulous taste, and are very sparingly soluble in water, still less soluble in alcohol. Its solution is acid, and dissolves many

metallic oxides with formation of double tartrates. When boiled with antimony trioxide, it forms tartar emetic.

It is used in the household, combined with monosodic carbonate, in baking, the two substances reacting upon each other to form Rochelle salt with liberation of carbon dioxide.

Baking-powders are now largely used as substitutes for yeast in the manufacture of bread. Their action is based upon the decomposition of hydrosodic carbonate by some salt having an acid reaction, or by a weak acid. In addition to the bicarbonate and flour, or corn-starch (added to render the bulk convenient to handle and to diminish the rapidity of the reaction), they contain cream of tartar, tartaric acid, alum, hydrochloric acid, or acid phosphates. Sometimes ammonium sesquicarbonate is used, in whole or in part, in place of sodium carbonate.

The reactions by which the carbon dioxide is liberated are the following:

1. $C_4H_4O_6HK + CO_3NaH = C_4H_4O_6NaK + H_2O + CO_2$.
   Hydropotassic tartrate. Hydrosodic carbonate. Sodium potassium tartrate. Water. Carbon dioxide.

2. $C_4H_4O_6H_2 + 2CO_3NaH = C_4H_4O_6Na_2 + 2H_2O + 2CO_2$
   Tartaric acid. Hydrosodic carbonate. Disodic tartrate. Water. Carbon dioxide.

3. $(SO_4)_3Al_2SO_4K_2 + 6CO_3NaH = SO_4K_2 + 3SO_4Na_2 + Al_2H_6O_6 + 6CO_2$.
   Aluminium potassium alum. Hydrosodic carbonate. Potassic sulphate. Sodic sulphate. Aluminium hydrate. Carbon dioxide.

4. $(SO_4)_3Al_2 + 6CO_3NaH = 3SO_4Na_2 + Al_2H_6O_6 + 6CO_2$.
   Aluminium sulphate. Hydrosodic carbonate. Sodic sulphate. Aluminium hydrate. Carbon dioxide.

5. $HCl + CO_3NaH = NaCl + H_2O + CO_2$.
   Hydrochloric acid. Hydrosodic carbonate. Sodium chloride. Water. Carbon dioxide.

6. $PO_4NaH_2 + CO_3NaH = PO_4Na_2H + H_2O + CO_2$.
   Monosodic phosphate. Hydrosodic carbonate. Disodic phosphate. Water. Carbon dioxide.

7. $2(SO_4)_3Al_2 + 3[2(CO_3[NH_4]_2)CO_2] + 6H_2O = 6SO_4(NH_4)_2 + 2Al_2H_6O_6 + 9CO_2$.
   Aluminium sulphate. Ammonium sesquicarbonate. Water. Ammonium sulphate. Aluminium hydrate. Carbon dioxide.

No. 1 is the reaction which takes place when cream of tartar and soda, or a baking-powder composed of those substances, are used in baking. The solid product of the reaction is Rochelle salt. No. 2 is that which occurs between tartaric acid and soda, and is but seldom utilized. No. 3 is that between burnt potassium alum and soda. It is not utilized at present, as the ammonium alum is more economical. No. 4 is that which occurs in alum baking-powders, the burnt ammonia alum being practically aluminium sulphate. The solid residues of the reaction are sodic sulphate and aluminium hydrate. No. 5 is a reaction very little used, owing to the inconvenience of handling a liquid, to the too rapid action

of the substances upon each other, and to the danger of introducing arsenic with the acid. No. 6 is used to a certain extent, and has the advantage that the solid residue of the reaction is a normal constituent of the body. No. 7 is occasionally utilized as an adjunct to No. 3.

In our opinion, while yeast is to be preferred to any baking-powder, an alum-powder is in no way more liable to produce disturbances of digestion than one compounded of cream of tartar and soda. Referring to Equation 4, above, and taking the amount of powder generally used, 35 grains per pound of bread, it will be seen that that amount of powder, containing 9.26 grains of aluminium sulphate, when neutralized during baking, produces 11.5 grains of Glauber's salt, 4.24 grains of aluminium hydrate, and 7.12 grains of carbon dioxide. On the other hand, a cream of tartar powder to produce, according to reaction above, the same quantity, 7.12 grains, of carbon dioxide, forms at the same time 33.98 grains of Rochelle salt. Assuming that one to two pounds is the average amount of bread consumed by an adult in twenty-four hours, there can be but little choice between taking on the one hand 4.24—8.48 grains of alumina and 11.5—23.0 grains of Glauber's salt; and on the other hand, 33.98—67.96 grains of Rochelle salt. Indeed, there is more danger to be apprehended from the tendency of repeated small doses of Rochelle salt to render the urine alkaline and thus favor the formation of phosphatic calculi, than from any supposed deleterious action of alumina, whose local action, even in considerable doses, is that of a very mild astringent, and whose absorption is very doubtful.

Sodium potassium tartrate—Rochelle salt—Sel de seignette—Potassii et sodii tartras (U. S.)—*Soda tartarata* (Br.)—$C_4H_4O_6NaK+4Aq.$—is prepared by saturating hydropotassic tartrate with sodium carbonate. It crystallizes in large, transparent prisms, which effloresce superficially in dry air and attract moisture in damp air. It fuses at 70—80°, and loses 3 Aq. at 100°. It is soluble in water, the solutions being dextrogyrous, $[a]_D=+29.67°$.

Potassium antimonyl tartrate—Tartarated antimony—Tartar emetic—Antimonii et potassii tartras (U. S.)—*Antimonium tartaratum*—(Br.)—$C_4H_4O_6K(SbO)'$—is prepared by boiling a mixture of 3 parts antimony trioxide and 4 parts hydropotassic tartrate in water for an hour, filtering, and allowing to crystallize; when required pure, it must be made from pure materials.

It crystallizes in transparent, right rhombic octohedra, which turn white in air. It dissolves in 19 parts of water at 8.7°, and in 2.8° parts at 100°. Its solutions are acid in reaction, have a nauseating, metallic taste, are lævogyrous, $[a]_D=+156.2°$, and are precipitated by alcohol. The crystals contain $\frac{1}{2}$ Aq., which they lose entirely at 100°, and partially by exposure to air. It is decomposed by the alkalies, alkaline earths, and alkaline carbonates, with precipitation of antimony trioxide. The precipitate is redissolved by excess of soda or potash, or by tartaric acid. Hydrochloric, sulphuric, and nitric acids precipitate corresponding antimonyl compounds from solutions of tartar emetic. It converts mercuric into mercurous chloride. It forms double tartrates with the tartrates of the alkaloids.

Cyanide, CNK or KCy—is usually obtained from the ferrocyanide. The dried salt is mixed with dry potassium carbonate; the mixture is thrown into a red-hot iron crucible, and heated as long as effervescence continues; the fused mass is then decanted from the precipitated iron and allowed to solidify.

It is usually met with in dull, white, amorphous masses; odorless when dry, it has the odor of hydrocyanic acid when moist. It is deliquescent, and very soluble in water; almost insoluble in alcohol. Its solution is acrid, and bitter in taste, with an after-taste of hydrocyanic acid. It is very readily oxidized to the cyanate, a property which renders it valuable as a reducing agent. Solutions of potassium cyanide dissolve iodine, silver chloride, the cyanides of silver and gold, and many metallic oxides.

It is actively poisonous, and produces its effects by decomposition and liberation of hydrocyanic acid (*q. v.*).

FERROCYANIDE—*Yellow prussiate of potash—Potassii ferrocyanidum* (U. S.)—*Potassæ prussias flava* (Br.)—$[Fe(CN)_6]K_4+3Aq$. This salt, the source of the other cyanogen compounds, is manufactured by adding organic matter (blood, bones, hoofs, leather, etc.) and iron to potassium carbonate in fusion; or by other processes in which the nitrogen is obtained from the residues of the purification of coal-gas, from atmospheric air, or from ammoniacal compounds.

It forms soft, flexible, lemon-yellow crystals, permanent in air at ordinary temperatures. They begin to lose water at 60°, and become anhydrous at 100°. Soluble in 2 parts of boiling water, and in 4 parts of cold water; insoluble in alcohol, which precipitates it from its aqueous solution. When calcined with potassium hydrate or carbonate, potassium cyanide and cyanate are formed, and iron is precipitated. Heated with dilute sulphuric acid, it yields an insoluble, white or blue salt, potassium sulphate, and hydrocyanic acid. Its solutions form with those of many of the metallic salts, insoluble ferrocyanides; those of zinc, lead and silver are white, cupric ferrocyanide is mahogany-colored, ferrous ferrocyanide is bluish white, ferric ferrocyanide (Prussian blue), is dark blue. Blue ink is a solution of Prussian blue in a solution of oxalic acid.

FERRICYANIDE—*Red prussiate of potash*—$Fe_2(CN)_{12}K_6$—is prepared by acting upon the ferrocyanide with chlorine; or, better, by heating the white residue of the action of sulphuric acid upon potassium ferrocyanide, in the preparation of hydrocyanic acid, with a mixture of 1 volume of nitric acid and 20 volumes of water; the *blue* product is digested with water and potassium ferrocyanide, the solution filtered and evaporated.

It forms red, oblique, rhombic prisms, almost insoluble in alcohol. With solutions of ferrous salts it gives a dark blue precipitate, *Turnbull's blue.*

Analytical characters.—*Platinic chloride* in the presence of hydrochloric acid, yellow precipitate, crystalline if formed slowly; sparingly soluble in water, much less in alcohol. *Tartaric acid* in not too dilute solution, white precipitate, soluble in alkalies and concentrated acids. *Hydrofluosilicic acid,* translucent, gelatinous precipitate; forms slowly, soluble in potash and in strong alkalies. *Perchloric acid,* white precipitate, sparingly soluble in water; insoluble in alcohol. *Phosphomolybdic acid,* white precipitate; forms slowly. Colors the flame of the Bunsen burner violet (the color is only observable in the presence of sodium through blue glass), and exhibits two bright lines, one in the red, one in the violet: $\lambda=7680$ and 4045.

Action of the sodium and potassium compounds upon the economy.—The hydrates of sodium and of potassium, and in a less degree the carbonates, disintegrate animal tissues, dead or living, with which they come in contact, and, by virtue of this action, act as powerful caustics upon a living tissue. Upon the skin they produce a soapy

feeling and in the mouth a soapy taste. Like the acids, they cause death, either immediately, by corrosion or perforation of the stomach; or secondarily after weeks or months, by closure of one or both openings of the stomach, due to thickening consequent upon inflammation.

The treatment consists in the neutralization of the alkali by an acid, dilute vinegar, or lemon-juice; or by an oil, olive-oil—or milk, with which it forms a soap.

The other compounds of sodium, if the acid be not poisonous, are without deleterious action, unless taken in excessive quantity. Common salt has produced paralysis and death in a dose of half a pound. The neutral salts of potassium, on the contrary, are by no means without true poisonous action when taken internally, or injected subcutaneously in sufficient quantities, causing dyspnœa, convulsions, arrest of the heart's action, and death. In the adult human subject, death has followed the ingestion of doses of ʒ ss.— ʒ j. of the nitrate, in several instances; doses of ʒ ij.— ʒ ij. of the sulphate, have also proved fatal.

SILVER.

Argentum.....Ag.....107.93

Although silver is usually classed with the "noble metals," it differs from gold and platinum widely in its chemical characters, in which it closely resembles the alkaline metals.

When pure silver is required, coin silver is dissolved in nitric acid and the diluted solution precipitated with hydrochloric acid. The silver chloride is washed until the washings no longer precipitate with silver nitrate; and reduced either: 1st, by suspending it in dilute sulphuric acid in a platinum basin, with a bar of pure zinc, and washing thoroughly after complete reduction; or, 2d, by mixing it with chalk and charcoal (AgCl, 100 parts, C, 5 parts, Co_3Ca, 70 parts) and gradually introducing the mixture into a red-hot crucible.

Silver is a white metal; sp. gr. 10.47—10.54; fusible at 1000°; very malleable and ductile; the best known conductor of heat and electricity. It is not acted on by pure air, but is blackened in air containing a trace of hydrogen sulphide. Chlorine, bromine, iodine, sulphur, selenium, phosphorus, and arsenic combine with it directly. Hot sulphuric acid dissolves it as sulphate, and nitric acid as nitrate. The caustic alkalies do not affect it. It alloys readily with many metals; its alloy with copper is harder than the pure metal.

Oxides.—Three oxides of silver are known: Ag_4O, Ag_2O, and Ag_2O_3.

Silver monoxide—Protoxide—Argenti oxidum (U. S., Br.)—Ag_2O—formed by precipitating a solution of silver nitrate with potash. It is a brownish powder; faintly alkaline and very slightly soluble in water; strongly basic. It readily gives up its oxygen. On contact with ammonium hydrate it forms a fulminating powder.

Chloride, AgCl—formed when hydrochloric acid or a chloride is added to a solution containing silver. It is white; turns violet and black in sunlight; volatilizes at 260°; sparingly soluble in hydrochloric acid; soluble in solutions of the alkaline chlorides, hyposulphites, and cyanides, and in ammonium hydrate.

Bromide, AgBr, and **Iodide,** AgI—are yellowish precipitates, formed by decomposing silver nitrate with potassium bromide and iodide.

Salts.—NITRATE—*Argenti nitras* (U. S., Br.)—NO_3Ag—is prepared by dissolving silver in nitric acid, evaporating, fusing, and recrystallizing. It crystallizes in anhydrous, right rhombic plates; soluble in one part of cold water, in 0.5 part of boiling water. The solutions are colorless and neutral. In the presence of organic matter it turns black. The fused salt, cast into cylindrical moulds, furnishes the *Argenti nitras fusa* (U. S.), *lapis infernalis*, or *lunar caustic* of pharmacy. If, during fusion, the temperature be raised too high, it is first decomposed into nitrite, oxygen, and silver, and, finally, leaves pure silver.

Dry chlorine and iodine decompose it with liberation of anhydrous nitric acid. It absorbs ammonia to form a white substance, NO_3Ag, $3NH_3$, which, when heated, gives up its ammonia. Its solution is decomposed very slowly by pure hydrogen, with deposition of silver.

Silver nitrate is used in photography, in the manufacture of hair-dyes, and of marking-ink, and in the silvering of glass.

CYANIDE—*Argenti cyanidum* (U. S.)—AgCN—is prepared by passing hydrocyanic acid through a solution of silver nitrate. It is a white, tasteless powder; gradually turns brown on exposure to light; insoluble in dilute acids; soluble in ammonium hydrate, and in solutions of ammoniacal salts, cyanides, and of sodium hyposulphite. The mineral acids decompose it with liberation of hydrocyanic acid.

Analytical Characters.—*Hydrochloric acid*, white, flocculent precipitate, insoluble in nitric acid, readily soluble in ammonium hydrate. *Potash* or *soda*, brown precipitate, insoluble in excess, soluble in ammonium hydrate. *Ammonium hydrate*, from neutral solutions, brown precipitate, soluble in excess. *Hydrogen sulphide* or *ammonium sulphydrate*, black precipitate, insoluble in the last-named reagent. *Potassium bromide*, yellowish white precipitate, insoluble in acids, if not very abundant, soluble in ammonium hydrate. *Potassium iodide*, same as bromide, but less soluble in ammonium hydrate.

Action on the economy.—Silver nitrate acts both locally as a corrosive, and systematically as a true poison. Its local action is due to its decomposition by contact with organic substances, resulting in the separation of elementary silver, whose deposition causes a black stain, and liberation of free nitric acid, which acts as a caustic. When absorbed, it causes nervous symptoms, referable to its poisonous action. The blue coloration of the skin, observed in those to whom it is administered for some time, is due to the reduction of the metal under the combined influence of light and organic matter; especially of the latter, as the darkening is observed, although it is less intense, in internal organs.

In acute poisoning by silver nitrate, sodium chloride or white of egg should be given; and, if the case be seen before the symptoms of corrosion are far advanced, emetics.

AMMONIUM COMPOUNDS.

Ammonium.....(NH_4)

Although the radical ammonium has probably never been isolated, there can remain but little doubt that such a radical exists in combination in the ammoniacal compounds. The ammonium hypothesis is based upon the following facts: 1st, when ammonia gas comes in contact with an acid gas, the two unite, without liberation of hydrogen, to form an ammoni-

acal salt; 2d, the diatomic anhydrides unite directly with dry ammonia, with formation of the ammonium salt of an amido-acid:

$$\underset{\text{Sulphur trioxide.}}{SO_3} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Ammonium sulphamate.}}{SO_3(NH_2)(NH_4)}$$

3d, when solutions of the ammoniacal salts are subjected to electrolysis, a mixture having the composition NH_3+H is given off at the negative pole; 4th, amalgam of sodium, in contact with a concentrated solution of ammonium chloride, increases much in volume, and is converted into a light, soft mass, having the lustre of mercury. This *ammonium amalgam* is decomposed gradually, giving off ammonia and hydrogen in the proportion NH_3+H; 5th, if the gases NH_3+H, given off by decomposition of the amalgam, exist there in simple solution, the liberated hydrogen would have the ordinary properties of that element; if, on the other hand, they exist in combination, the hydrogen would exhibit the more energetic affinities of an element in the nascent state. The hydrogen so liberated is in the nascent state.

Oxide and Hydrate.—Neither the oxide of ammonium $(NH_4)_2O$, nor its hydrate, NH_4HO, has as yet been isolated, both being probably decomposed into ammonia and water immediately they are liberated.

The hydrate, NH_4HO—is considered as existing in the so-called aqueous solutions of ammonia, which are clear liquids, lighter than water, have the taste and odor of ammonia, and are strongly alkaline in reaction. The *Aqua ammoniæ fortior* (U. S.) is of sp. gr. 0.900, and contains 249.5 grams NH_3 per litre; that of the British Pharmacopœia is of sp. gr. 0.891, and contains 277 grams NH_3 per litre. The *Aqua ammoniæ* (U. S.) is of sp. gr. 0.960, and contains 93.1 grams NH_3 per litre; that of the British Pharmacopœia is of sp. gr. 0.950, and contains 118.0 grams NH_3 per litre.

Sulphides.—Ammonium forms four sulphides $(NH_4)_2S$, $(NH_4)_2S_2$, $(NH_4)_2S_4$, and $(NH_4)_2S_5$; and a sulphydrate $(NH_4)HS$.

The *sulphydrate,* NH_4HS—is formed in solution, for use as a reagent in analysis, by saturating an aqueous solution of ammonium hydrate, protected from air, with hydrogen sulphide.

The sulphides of ammonium are also formed during the decomposition of nitrogenous organic substances, and exist in the gases discharged from burial-vaults, sewers, etc.

Chloride—*Muriate of ammonia—Sal-ammoniac—Ammonii chloridum* (U. S., Br.)—NH_4Cl—is obtained from the ammoniacal water of gas-works, which contains ammonium carbonate and tarry substances. It is a translucid, fibrous, and elastic solid, salty in taste and neutral in reaction; volatilizes without fusion and without decomposition; 100 parts of water dissolve 37.28 parts of the salt at 20°, and 77.24 parts at 110°. Its solutions are neutral, but lose ammonia and become acid when boiled.

Ammonium chloride exists in minute quantities in the gastric juice of the sheep and dog. It has also been said to occur in the perspiration, urine, saliva, and tears, which contain some ammonium compound in small quantity, but whether it is the chloride or another is not determined with certainty.

Bromide—*Ammonii bromidum* (U. S., Br.), NH_4 (Br.)—is formed either by combining ammonia and hydrobromic acid; or by decomposing ferrous bromide with aqua ammoniæ; or by double decomposition between potassium bromide and ammonium sulphate. It is a white, granu-

lar powder, or in large prisms, which turn yellow on exposure to air; soluble in 1.29 parts of water. It volatilizes without decomposition. It contains 81.63 per cent. of bromine.

Iodide—*Ammonii iodidum* (U. S.), NH_4I—is formed by the union of equal volumes of ammonia and hydriodic acid, or by double decomposition of potassium iodide and ammonium sulphate. It crystallizes in cubes; deliquescent; soluble in 0.60 parts of water. It contains 87.58 per cent. of iodine.

Salts of ammonium.—NITRATE—*Ammonii nitras* (U. S.)—$NO_3(NH_4)$—is prepared by neutralizing nitric acid with ammonium hydrate or carbonate. It forms flexible, anhydrous, six-sided prisms; soluble in 0.5 parts of water at 18°; fuses at 150°, and decomposes at 210° with formation of nitrous oxide: $NO_3(NH_4)=N_2O+2H_2O$. Ammonia and nitrogen di- and tetroxides are also formed if the heat be suddenly applied or allowed to rise too high. When fused it is an active oxidant.

SULPHATES. — *Ammonic sulphate — Diammonic sulphate — Neutral ammonium sulphate—Ammonii sulphas* (U. S.)—$SO_4(NH_4)_2$—is manufactured from the ammoniacal gas liquids. These are distilled with milk of lime, and the product directed into dilute sulphuric acid; or the crude liquid is passed through filters charged with gypsum, when calcium carbonate and ammonium sulphate are formed. It forms anhydrous rhombic crystals, quite soluble in water; fuses at 140°, and is decomposed at 200° into ammonia and mono-ammonic sulphate.

Hydro-ammonic sulphate—Mono-ammonic sulphate—Bisulphate of ammonia, $SO_4H(NH_4)$—is formed by the action of sulphuric acid upon diammonic sulphate. It crystallizes in right rhombic prisms, soluble in water and in alcohol.

ACETATE—$C_2H_3O_2(NH_4)$—is formed by saturating acetic acid with ammonia, or with ammonium carbonate. It is white, odorless, very soluble in water and in alcohol; fuses at 86°, and gives off ammonia, then acetic acid, and finally acetamide. Its aqueous solution is used in medicine under the names *Liq. ammonii acetatis; Spirit of Mindererus.*

CARBONATES.—*Ammonic carbonate—Diammonic carbonate—Neutral ammonium carbonate*, $CO_3(NH_4)_2+Aq.$—has recently been prepared as a crystalline solid. When exposed to air it is decomposed into ammonia and the monoammonic salt.

Hydroammonic carbonate—Monoammonic carbonate—Acid carbonate of ammonia, $CO_3H(NH_4)$—is prepared by saturating a solution of ammonium hydrate or sesquicarbonate with carbon dioxide. It crystallizes in large, rhombic prisms; soluble to the extent of 21 parts in 100 in water at 20°; at 60° it is decomposed into ammonia and carbon dioxide.

Ammonium sesquicarbonate—Sal volatile—Ammonii carbonas (U. S.) —*Ammoniæ carbonas* (Br.)—$(CO_3)_2(NH_4)_4H_2+Aq.$—the commercial carbonate of ammonia, prepared by heating a mixture of ammonium chloride and chalk, and condensing the product; crystallizes in rhombic prisms; has an ammoniacal odor and an alkaline reaction; soluble to the extent of 25 parts in 100 of water at 13°. By exposure to air or by heating its solution, it is decomposed into water, ammonia, and monoammonic carbonate.

Analytical characters.—The compounds of ammonium are odorless and entirely volatile at moderately elevated temperatures. Heated with potash, they give off ammonia, recognizable, 1st, by changing moist, red litmus paper blue; 2d, by its odor; and, 3d, by forming white clouds on contact with a glass rod moistened with hydrochloric acid.

With *platinic chloride*, a yellow, crystalline precipitate. With *hydrosodic tartrate* in moderately concentrated and neutral solutions, a white, crystalline precipitate.

Action on the Economy.—Solutions of the hydrate and carbonate act upon animal tissues in the same way as do the corresponding potassium and sodium compounds. They, moreover, disengage gaseous ammonia, which rapidly causes intense dyspnœa, irritation of the air-passages, and suffocation.

The treatment indicated is the neutralization of the alkali by a dilute acid. Usually the vapor of acetic acid or of dilute hydrochloric acid must be administered by inhalation.

III. CALCIUM GROUP.

Metals of the Alkaline Earths.

CALCIUM, Ca, 40; STRONTIUM, Sr, 87.5; BARIUM, Ba, 137.2.

The members of this group are divalent in all their compounds; each forms two oxides, MO and MO_2; each forms a hydrate possessed of well-marked basic properties.

CALCIUM.

Ca.....40

Calcium is a light yellow metal; hard, very ductile; fusible at a red heat; not sensibly volatile; sp. gr. 1.984. It is not altered in dry air, but is converted into the hydrate in moist air.

Oxides.—*Calcium protoxide—Quick-lime—Calx* (U. S., Br.)—CaO—is prepared industrially by heating a natural calcium carbonate; when required pure, by heating a carbonate, obtained by precipitation.

It occurs in white or grayish, amorphous masses, odorless, alkaline and caustic; sp. gr. 2.3; almost infusible. With water, it is converted into the hydrate; the union is attended with great elevation of temperature, and is known as *slaking*. In air, lime becomes *air-slaked*, and is converted into a white powder, a hydrocarbonate, CO_3Ca,CaH_2O_2.

Calcium hydrate—Slacked lime—Calcis hydras (Br.)—CaH_2O_2—is prepared by the action of water upon quick-lime. If the quantity of water used be one-third that of the oxide, the hydrate is formed as a dry, white powder, odorless, alkaline in taste and reaction. It is more soluble in cold than in hot water.

Lime-water—Liquor calcis (U. S., Br.)—is a solution of the hydrate in water. The solubility of calcium hydrate is diminished by the alkalies, and is increased by sugar and mannite. The *Liq. calcis saccharatus* (Br.) is a solution of the hydrate, or of calcium saccharate, in solution of cane-sugar. *Milk of lime* is lime-water with an excess of hydrate. Calcium hydrate absorbs carbon dioxide.

Chloride—*Calcii chloridum* (U. S., Br.)—$CaCl_2+6Aq$.—is obtained by dissolving marble in hydrochloric acid; is a bitter substance; deliquescent and very soluble in water; when fused it loses all its Aq. and forms a white, amorphous mass; used as a drying agent.

Chloride of lime—Bleaching-powder—Calx chlorinata (U. S.)—*Calx chlorata* (Br.)—is a mixture composed principally of calcium chloride, $CaCl_2$, and hypochlorite, $(ClO)_2Ca$; prepared by passing chlorine over slaked lime maintained in excess. It is a grayish white powder, having a bitter, acrid taste; soluble in cold water; decomposed by boiling water; readily decomposed, with liberation of chlorine, by the weakest acids; carbon dioxide decomposes it with formation of calcium carbonate and liberation of hypochlorous acid, if it be moist; or of chlorine, if it be dry.

Salts.—SULPHATE, SO_4Ca.—The hydrated compound, $SO_4Ca+2Aq.$, occurs as *gypsum*, in right rhombic prisms; frequently grouped in arrow-head shaped macles; sparingly soluble in water; more soluble in water containing free acid or chlorides; insoluble in alcohol. Ground gypsum is used in the arts under the name *terra alba*. At 80°, or more rapidly between 120° and 130°, it loses its Aq. and is converted into an opaque, white mass, which, when ground, is *plaster-of-Paris*.

The *setting* of plaster when mixed with water is caused by the conversion of the anhydrous into the crystalline, hydrated salt. Plaster surfaces are rendered smooth, dense, and capable of taking a high polish by adding glue and alum, or an alkaline silicate, to the water.

PHOSPHATES.—Three phosphates of calcium are known: $(PO_4)_2Ca_3$, $(PO_4H)_2Ca_2$, and $(PO_4H_2)_2Ca$.

Tricalcic phosphate—Tribasic or *neutral phosphate—Bone phosphate—Calcis phosphas præcipitata* (U. S.)—*Calcis phosphas* (Br.)—$(PO_4)_2Ca_3$—This salt occurs in soils, in *coprolites*, in guano, in all plants, and in every tissue and fluid of animal bodies. It is obtained by dissolving bone-ash in hydrochloric acid, filtering, and precipitating with ammonium hydrate; or by double decomposition between calcium chloride and an alkaline phosphate. When freshly precipitated it is gelatinous; when dry, it is a light, white, amorphous powder; almost insoluble in pure water; soluble to a slight extent in water containing ammoniacal salts, or chloride or nitrate of sodium; readily soluble in dilute acids, even in water charged with carbon dioxide. Sulphuric acid decomposes it into calcium sulphate and monocalcic phosphate. *Bone-ash* is an impure tricalcic phosphate, used in the manufacture of phosphorus and of superphosphate (see below).

Dicalcic phosphate, $(PO_4H)_2Ca_2+2H_2O$—a crystalline, insoluble salt; formed by double decomposition between calcium chloride and disodic phosphate in acid solution.

Monocalcic phosphate—Acid calcium phosphate—Superphosphate of lime—$(PO_4H_2)_2Ca$—exists in brain-tissue and in acid animal fluids. It is formed when the tricalcic salt is dissolved in an acid, and is manufactured for use as a manure, by decomposing bone-ash with sulphuric acid. It crystallizes in pearly plates; very soluble in water, the solution being acid.

Physiological.—All three calcium phosphates, accompanied by the corresponding magnesium salts, exist in the animal economy. The *tricalcic* salt occurs in all the solids of the body and in all fluids not having an acid reaction, being held in solution in the latter by the presence of chlorides. In the fluids it is present in very small quantity, except in the milk, in which it is comparatively abundant; 2.5 to 3.95 parts per 1,000 in human milk, and 1.8 to 3.87 parts per 1,000 in cow's milk; constituting about 70 per cent. of the ash. The *bones* contain about 35 parts of organic matter, combined with 65 parts of mineral material. The average

composition of human bone-ash is tricalcic phosphate, 83.89; calcium carbonate, 13.03; calcium combined with chlorine, fluorine, and organic acids, 0.35; fluorine, 0.23; chlorine, 0.18. The average quantity of tricalcic phosphate in male adult bones is 57 per cent.; that of calcium carbonate, 10 per cent.; and that of trimagnesic phosphate, 1.3 per cent. In pathological conditions the composition of bone is modified as shown in the following table:

ANALYSES OF BONES.

In 100 parts.	Healthy male, aged 40; femur.	Osteomalacia, male, aged 40; femur.	Osteomalacia, male, aged 60; femur.	Osteomalacia, child; vertebra.	Rachitis; femur.	Rachitis; humerus.	Caries; femur.	Caries, female, aged, 40; vertebra.	Necrosis.
Collagen	.....	48.83	32.54	75.22	72.20	81.12	25.69	41.42	19.58
Fats	.....	29.18	4.15	6.12	7.20		3.00	8.36	1.23
Tricalcic phosphate	56.9	17.56	58.25	12.56	14.78	15.60	51.53	44.05	72.63
Calcium fluoride	.....	.....	.....	.....	1.00	.....			
Calcium carbonate	10.2	3.04	7.49	3.20	3.00	2.66	5.44	3.45	4.03
Trimagnesic phosphate	1.3	0.23	1.22	0.92	0.80	*	3.43	1.02	1.96
Other salts	.....	0.37	1.35	1.98	1.02	0.62	0.91	1.70	0.61
Organic matter	35.8	78.01	36.69	81.34	79.40	81.12	38.69	49.78	20.80
Ash	64.2	21.20	63.31	19.66	20.60	18.88	61.31	50.22	79.20
* Included in tricalcic phosphate.	Frémy.	Lehmann.	Von Bibra.	Marchand.	Marchand.	Ragsky.	Becquerel and Rodier.	Becquerel and Rodier.	Von Bibra.

The *teeth* consist largely of tricalcic phosphate. Von Bibra gives for the enamel of the molars in man, 89.82 per cent. of this salt, and for the dentine, 66.72 per cent.

From the *urine*, tricalcic phosphate is frequently deposited, either in the form of an amorphous, granular sediment, or as calculi. The *dicalcic* salt occurs occasionally in urinary sediments, in the form of needle-shaped crystals arranged in rosettes, and also in urinary calculi. The *monocalcic* salt is always present in acid *urine*, constituting, with the corresponding magnesium salt, the *earthy phosphates*. The total elimination of phosphoric acid by the urine is about 2.75 grams in twenty-four hours, of which two-thirds is in combination with alkaline metals, and one-third in the phosphates of calcium and magnesium. The hourly elimination follows about the same variation as that of the chlorides. The total elimination is greater with animal than with vegetable food; is diminished during pregnancy; and is above the normal during excessive mental work. The elimination of earthy phosphates is greatly increased in osteomalacia, often so far that they are in excess of the alkaline phosphates.

So long as the urine is *acid*, it contains the soluble acid phosphates; when the reaction becomes alkaline, or even on loss of carbon dioxide by exposure to air, the acid phosphate is converted into the insoluble tricalcic phosphate. Alkaline urines are for this reason almost always turbid, and become clear on the addition of acid. It is in such urine that phosphatic calculi are invariably formed, usually about a nucleus of uric acid or of a foreign body. If the alkalinity be due to the formation of ammonia, the trimagnesic phosphate is not formed, but ammonio-magnesium phosphate (*q. v.*).

A process for determining the quantity of phosphates in urine is

based upon the formation of the insoluble uranium phosphate, and upon the production of a brown color when a solution of a uranium salt is brought in contact with a solution of potassium ferrocyanide. Four solutions are required: 1st, *a standard solution of disodic phosphate;* made by dissolving 10.085 grams of crystallized, non-effloresced disodic phosphate in water, and diluting to a litre; 2d, *an acid solution of sodium acetate,* made by dissolving 100 grams sodium acetate in water, adding 100 c.c. glacial acetic acid, and diluting with water to a litre; 3d, *a strong solution of potassium ferrocyanide;* 4th, *a standard solution of uranium acetate,* made by dissolving 20.3 grams of yellow uranic oxide in glacial acetic acid, and diluting with water to nearly a litre. Solution 1 serves to determine the true strength of this solution, as follows: 50 c.c. of Solution 1 are placed in a beaker, 5 c.c. of Solution 2 are added, the mixture heated on a water-bath, and the uranium solution gradually added from a burette until a drop from the beaker produces a brown color when brought in contact with a drop of the ferrocyanide solution. At this point the reading of the burette, which indicates the number of c.c. of the uranium solution, corresponding to 0.1—P_2O_5, is taken. A quantity of water, determined by calculation from the result thus obtained, is then added to the remaining uranium solution, such as to render each cubic centimetre equivalent to 0.005 gram phosphoric anhydride.

To determine the *total phosphates* in a urine: 50 c.c. are placed in a beaker, 5 c.c. sodium acetate solution are added; the mixture is heated on the water-bath, and the uranium solution delivered from a burette until a drop, removed from the beaker and brought in contact with a drop of ferrocyanide solution, produces a brown tinge. The burette reading, multiplied by 0.005, gives the amount of phosphoric anhydride in 50 c.c. urine; and this, multiplied by $\frac{1}{50}$ the amount of urine passed in 24 hours, gives the daily elimination.

To determine the *earthy phosphates,* a sample of 100 c.c. urine is rendered alkaline with ammonia and set aside for 12 hours; the precipitate is then collected upon a filter, washed with ammoniacal water, brought into a beaker, dissolved in a small quantity of acetic acid; the solution diluted to 50 c.c. with water, treated with 5 c.c. sodium acetate solution, and the amount of phosphoric anhydride determined as above.

CARBONATES. — *Calcium carbonate — Calcis carbonas præcipitata* (U. S., Br.)—CO_3Ca—the most abundant of the natural compounds of calcium, exists as *limestone, calk spar, chalk, marble, Iceland spar,* and *arragonite,* and forms the mineral basis of the corals, shells of crustacea, and of molluscs, etc.

The *precipitated chalk, Calcii carbonas præcipitata* (U. S., Br.), is prepared by precipitating a solution of calcium chloride with one of sodium carbonate. *Prepared chalk, Creta præparata* (U. S., Br.), is native chalk, purified by grinding with water, diluting, allowing the coarser particles to subside, decanting the still turbid liquid, collecting, and drying the finer particles; a process known as *elutriation.*

It is a white powder, almost insoluble in pure water; much more soluble in water containing carbonic acid, the solution being regarded as containing *hydrocalcic carbonate* $(CO_3)_2H_2Ca$. At a red heat it yields carbon dioxide and calcic oxide. It is decomposed by acids with liberation of carbon dioxide.

Physiological.—Calcium carbonate is much more abundant in the lower than in the higher forms of animal life. It occurs in the egg-shells

of birds, in the bones and teeth of all animals; in solution in the saliva and urine of the herbivora, and deposited in the crystalline form, as *otoliths*, in the internal ear of man. It is deposited pathologically in calcifications, in parotid calculi, and occasionally in human urinary calculi and sediments.

OXALATE—*Oxalate of lime*—C_2O_4Ca—exists in the sap of many plants, and is formed as a white, crystalline precipitate by double decomposition between a calcium salt and an alkaline oxalate. It is insoluble in water, acetic acid, or ammonium hydrate; soluble in the mineral acids and in solution of acid sodium phosphate.

Physiological.—Calcium oxalate is taken into the body in vegetable food, and is formed in the economy, where its production is intimately connected with that of uric acid.

It occurs in the urine, in which it is increased in quantity when large amounts of vegetable food are taken, when sparkling wines or beers are indulged in; and when the carbonates of the alkalies, lime-water, and lemon-juice, are administered. It is deposited as a urinary sediment in the form of small, brilliant octohedra, having the appearance of the backs of square letter-envelopes, or in dumb-bells. It is usually deposited from acid urine, and accompanied by crystals of uric acid. Sometimes, however, it occurs in urines undergoing alkaline fermentation, in which case it is accompanied by crystals of ammonio-magnesian phosphate.

The renal or vesical calculi of calcium oxalate, known as *mulberry calculi*, are dark brown or gray, very hard, occasionally smooth, generally tuberculated, soluble in hydrochloric acid without effervescence; and when ignited, they blacken, turn white, and leave an alkaline residue.

Analytical characters.—*Ammonium sulphydrate* nothing, unless the calcium salt be the phosphate, oxalate, or fluoride in acid solution, when it forms a white precipitate. *Alkaline carbonates*, white precipitate, not prevented by the presence of ammoniacal salts. *Ammonium oxalate*, white precipitate, insoluble in acetic acid; soluble in hydrochloric or nitric acid. *Sulphuric acid*, white precipitate, from solutions which are not too dilute; very sparingly soluble in water, insoluble in alcohol; soluble in sodium hyposulphite solution. *Sodium tungstate*, dense white precipitate, even from dilute solutions. Colors the flame of the Bunsen burner reddish yellow.

BARIUM.

Ba.....137.2

The element itself is not of interest.

Oxides.—BARIUM MONOXIDE—*Baryta*—BaO—is prepared, by calcining the nitrate, as a grayish white caustic earth. It unites readily with water to form a *hydrate*, BaH_2O_2, whose aqueous solution is *baryta water*.

Chloride—*Barii chloridum* (U. S.)—$BaCl_2+2$ Aq.—is obtained by treating the native sulphide, or carbonate, with hydrochloric acid. It forms crystalline plates, permanent in air, soluble in water.

Analytical characters.—*Alkaline carbonates*, white precipitate in alkaline solution. *Sulphuric acid*, or *calcium sulphate*, white precipitate, insoluble in acids. *Sodium phosphate*, white precipitate, soluble in nitric acid. Colors the Bunsen flame greenish yellow.

Action on the economy.—The oxides and hydrate act as corro-

sives by virtue of their alkalinity, and also as true poisons. All soluble compounds of barium, and those which are readily converted into soluble compounds in the stomach, are actively poisonous. Soluble sulphates, followed by emetics, are indicated as antidotes.

IV. MAGNESIUM GROUP.

MAGNESIUM, Mg, 24; ZINC, Zn, 65.2; CADMIUM, Cd, 112.

Each of these elements forms a single oxide—a corresponding basic hydrate, and a series of salts in which its atoms are divalent.

MAGNESIUM.

Mg.....24

Is prepared by heating its chloride with sodium. It is a white metal; sp. gr. 1.75; fuses at 1000°; burns with great brilliancy in air; decomposes vapor of water when heated; reduces carbon dioxide with the aid of heat; combines directly with chlorine, sulphur, phosphorus, arsenic, and nitrogen; dissolves in dilute acids, but is not affected by alkaline solutions.

Oxide—*Calcined magnesia*—*Magnesia* (U. S., Br.)—MgO—is obtained by calcining the carbonate, hydrate, or nitrate. Is a light, bulky, white powder, odorless, and tasteless; has an alkaline reaction; almost insoluble in water; dissolves readily in dilute acids without effervescence.

Hydrate—*Hydrated magnesia*—MgH_2O_2—is formed when a solution of a magnesium salt is precipitated with sodium hydrate in excess, in the absence of ammoniacal salts. It exists in mixtures holding it in suspension in water (*milk of magnesia*), used as antidotes to the effects of acid corrosives.

Chloride, $MgCl_2$—is obtained by dissolving the carbonate in hydrochloric acid. It is one of the most deliquescent substances known, and imperfectly purified table-salt containing it, along with calcium chloride, becomes damp on exposure to air.

Salts.—SULPHATE—*Epsom salt*—*Sedlitz salt*—*Magnesii sulphas* (U. S.)—*Magnesiæ sulphas* (Br.)—$SO_4Mg+7Aq$.—exists in solution in sea-water and in the waters of many mineral springs, especially in those belonging to the class of *bitter waters*. It is obtained artificially by the action of sulphuric acid upon magnesium carbonate. It crystallizes in rhombic needles; fuses and gradually loses water of crystallization up to 132°, when it retains 1 Aq., which is driven off at 210°. It dissolves in 0.8 parts of water at 19°.

PHOSPHATES.—These phosphates resemble those of calcium in their constitution and properties, and accompany them in the situations in which they occur in the animal body, but in much smaller quantity.

Magnesium also forms double phosphates, constituted by the substitution of one atom of the divalent metal for two of the atoms of basic hydrogen, of a molecule of phosphoric acid and of an atom of an alkaline metal, or of an ammonium group, for the remaining basic hydrogen.

One of these compounds is *ammonio-magnesian phosphate; triple phosphate*, $PO_4Mg(NH_4)+6Aq$.—which is formed when excess of an alkaline phosphate and of ammonia are added to a solution containing magnesium.

In the urine, alkaline phosphates and magnesium salts are always present, and consequently when, by decomposition of urea, the urine becomes alkaline, the conditions for the formation of this compound are fulfilled; and being practically insoluble, especially in the presence of excess of phosphates and of ammonia, it is deposited in crystals, usually tabular, sometimes feathery and stellate in form. When it is formed in the bladder, in the presence of some body to serve as a nucleus, the crystallization takes place upon the nucleus and a *fusible calculus* is produced.

SILICATES constitute a number of important minerals: *talc, steatite* or *soapstone, asbestos*, and *meerschaum.*

CARBONATES.—*Magnesium carbonate—Neutral carbonate*—CO_3Mg—exists in *magnesite*, and, combined with calcium carbonate, in *dolomite.* It cannot be formed, like most other carbonates, by decomposing a magnesium salt with an alkaline carbonate, but may be produced by passing carbon dioxide through water holding tetramagnesic tricarbonate in suspension. *Trimagnesic dicarbonate*, $2(CO_3Mg),MgH_2O_2+2H_2O$—is formed in small crystals when a solution of magnesium sulphate is precipitated with excess of sodium carbonate and the mixture boiled. *Tetramagnesic tricarbonate—Magnesia alba—Magnesii carbonas* (U. S.)—*Magnesiæ carbonas* (Br.)—$3(CO_3Mg),MgH_2O_2+3H_2O$—occurs in commerce in the form of light, white cubes, composed of a powder which is amorphous or partly crystalline. It is prepared by precipitating a solution of magnesium sulphate with one of sodium carbonate; if the precipitation occur in cold dilute solutions (*Magnesiæ carbonas lævis*, Br.), very little carbon dioxide is given off; a light, bulky precipitate falls, and the solution contains magnesium, probably in the form of the bicarbonate $(CO_3)_2H_2Mg.$; this solution, on standing, deposits crystals of the carbonate, $CO_3Mg+3Aq$. If hot concentrated solutions be used and the liquid then boiled upon the precipitate, carbon dioxide is given off, and a denser, heavier precipitate is formed, which varies in composition according to the length of time during which the boiling is continued, and to the presence or absence of excess of sodium carbonate. The pharmaceutical product is intended to have the composition given above; it frequently contains $4(CO_3Mg),MgH_2O_2+4H_2O$, or even $2(CO_3Mg),MgH_2O_2+2H_2O$. All of these compounds are very sparingly soluble in water, but much more soluble in water containing ammoniacal salts.

Analytical characters.—*Ammonium hydrate*, voluminous white precipitate from *neutral* solutions. *Potassium* or *sodium hydrate*, voluminous white precipitate from warm solutions; prevented by the presence of ammonium salts and of certain organic substances. *Ammonium carbonate*, slight precipitate from hot solutions; prevented by the presence of ammoniacal salts. *Sodium* or *potassium carbonate*, white precipitate, best from hot solution; prevented by the presence of ammoniacal compounds. *Disodic phosphate*, white precipitate in hot, not too dilute solutions. *Oxalic acid*, nothing alone, but in the presence of ammonium hydrate a white precipitate; not formed in the presence of the salts or chloride of ammonium.

ZINC.

Zn.....65.2

Is a bluish white metal; either crystalline, granular, or fibrous. Pure zinc is quite malleable and ductile; the commercial is usually brittle; at 130°—150° it is pliable; at 200°—210° it again becomes brittle; it fuses at 415°, and distils at 1040°; sp. gr. 6.862 if cast, 7.215 if rolled; at 500° it burns with a greenish flame and gives off snowy flakes of the oxide (*lana philosophica, pompholix*). In moist air it becomes coated with a hydrocarbonate. Pure sulphuric acid, SO_4H_2, is not affected by pure zinc in the cold; the commercial metal dissolves in the diluted acid with evolution of hydrogen; the action is more rapid in the presence of copper or platinum, less so in that of mercury. It also decomposes nitric, hydrochloric, and acetic acids.

When required in toxicological analysis, it must be free from arsenic, and, in some instances, from phosphorus. It is better to test samples until a pure one is found, than to attempt the purification of a contaminated metal.

Oxide—*Zinci oxidum* (U. S., Br.)—ZnO—is prepared either by calcining the precipitated carbonate, or by burning the metal in a current of air. An impure oxide, known as *tutty*, is deposited in the flues of zinc furnaces and in those in which brass is fused. When obtained by calcination of the carbonate, it forms a soft, white, tasteless, and odorless powder; when produced by burning the metal, it occurs in light, voluminous, white masses. It is neither fusible, volatile, nor decomposable by heat, and is completely insoluble in neutral solvents. It dissolves in dilute acids, with formation of the corresponding salts.

It is used in the arts as a white pigment in place of lead carbonate, and is not darkened by hydrogen sulphide.

Zinc hydrate, ZnH_2O_2—cannot be obtained by union of the oxide with water, but is formed when a solution of a zinc salt is precipitated by potash. It is, when freshly precipitated, very soluble in alkalies and in solutions of ammoniacal salts.

Chloride—*Butter of zinc—Zinci chloridum* (U. S., Br.)—$ZnCl_2$ + Aq.—is obtained by dissolving zinc in hydrochloric acid. It forms a soft, white mass; very deliquescent, fusible, and volatile; extremely soluble in water, freely soluble in alcohol; its solution has a burning, metallic taste, destroys vegetable tissues, dissolves silk, and exerts a strong, dehydrating action upon organic substances in general.

In dilute solution it is used as a disinfectant (*Burnett's fluid*), as a preservative of wood, and as an embalming injection.

Salts.—Sulphate—*White vitriol—Zinci sulphas* (U. S., Br.)—$SO_4Zn + nH_2O$—is formed when zinc, or its oxide, sulphide, or carbonate is dissolved in dilute sulphuric acid. It crystallizes below 30°, with 7 Aq.; at 30°, with 6 Aq.; between 40° and 50°, with 5 Aq.; at 0° from a concentrated, acid solution, with 4 Aq.; with 2 Aq., as a crystalline powder deposited from a boiling solution by the addition of concentrated sulphuric acid; with 1 Aq. from a saturated solution at 100°; finally, anhydrous, by heating the preceding to 238°.

The salt usually met with is that with 7 Aq., which is very soluble in water; insoluble in absolute alcohol, sparingly soluble in weak alcohol.

Its solutions have a strong, styptic taste; coagulate albumin when added in moderate quantity, the coagulum dissolving in an excess, and form insoluble precipitates with the tannins.

Analytical characters.—*Hydrate of potassium, sodium,* or *ammonium*—white precipitate, soluble in excess. *Potassium,* or *sodium carbonate,* white precipitate in the absence of ammoniacal salts. *Hydrogen sulphide,* in neutral solution, white precipitate; in presence of an excess of a mineral acid, this precipitation is prevented unless sodium acetate is also present. *Ammonium sulphydrate,* white precipitate, insoluble in excess, in potassium or ammonium hydrate, or in acetic acid; soluble in dilute mineral acids. *Ammonium carbonate,* white precipitate, soluble in excess. *Disodic phosphate,* in the absence of ammoniacal salts, white precipitate, soluble in acids or alkalies. *Potassium ferrocyanide,* white precipitate, insoluble in hydrochloric acid.

Action on the economy.—All the compounds of zinc which are soluble in the digestive fluids behave as true poisons; and solutions of the chloride (in common use by tinsmiths, and in disinfecting fluids) have also well-marked corrosive properties. When zinc compounds are taken, it is almost invariably by mistake for other substances: the sulphate for Epsom salt, and solutions of the chloride for various liquids, gin, fluid magnesia, vinegar, etc.

Metallic zinc is dissolved by solutions containing sodium chloride, or organic acids, for which reason articles of food kept in vessels of galvanized iron become contaminated with zinc compounds, and, if eaten, produce, more or less intense symptoms of intoxication. For the same reason materials intended for analysis, in cases of supposed poisoning, should never be packed in jars closed by zinc caps.

V. NICKEL GROUP.

Nickel, Ni, 59; Cobalt, Co, 59.

These two elements bear a certain resemblance to those of the iron group; from which they differ in forming, so far as known, no compounds similar to the ferrates, chromates, and manganates. They form compounds corresponding to the sesquioxide of iron, but the salts corresponding to the ferric series are wanting, or exceedingly unstable if they exist.

Analytical characters.—Nickel—*Ammonium sulphydrate,* black precipitate, insoluble in excess. *Potassium,* or *sodium hydrate,* apple-green precipitate in the absence of tartaric acid; insoluble in excess. *Ammonium hydrate,* apple-green precipitate, soluble in excess; this solution is violet and deposits the hydrate when heated with potash.

Cobalt.—*Ammonium sulphydrate,* brown-black precipitate, insoluble in excess. *Potash,* blue precipitate, turns red slowly in the cold; quickly if heated; not formed in the cold in the presence of ammoniacal salts. *Ammonium hydrate,* blue precipitate; turns red in the absence of air, green in its presence.

VI. COPPER GROUP.

COPPER, Cu, 63.5; MERCURY, Hg, 200.

Each of these elements forms two series of compounds; one of which contains the divalent group $\left(\begin{matrix}Cu\\|\\Cu\end{matrix}\right)''$ or $(Hg_2)''$ and is designated by the termination *ous;* the other contains the single, divalent atoms, and is designated by the termination *ic.*

COPPER.

Cuprum .....Cu 63.5

A yellowish red metal, dark brown when finely divided; sp. gr. 8.914—8.952; very malleable, ductile, and tenacious; a good conductor of heat and of electricity. It is unaltered in dry air; in damp air it is coated with a green basic carbonate; heated to redness in air, it is oxidized. Hot sulphuric acid dissolves it with liberation of sulphur dioxide; nitric acid, with liberation of nitrogen dioxide; and hot hydrochloric acid, with liberation of hydrogen. Weak acids form soluble salts with it in presence of air and moisture. Ammonium hydrate is colored blue by contact of air and copper.

Oxides.—CUPROUS OXIDE—*Suboxide or black oxide*—$(Cu_2)O$—is formed as a red or yellow powder, by calcining a mixture of cuprous chloride and sodium carbonate.

A yellow *hydrate* is precipitated when cupric salts are decomposed by boiling with glucose (Fehling's and Trommer's tests). It loses its water of hydration at 360°.

CUPRIC OXIDE—*Binoxide—Black oxide*—CuO—is prepared by heating copper to dull redness in a current of air, or by calcining its nitrate. It is also formed by the precipitation of a boiling solution of a cupric salt by potash, and prolonged boiling of the liquid on the precipitate.

It is black, or dark reddish brown, amorphous, and is reduced by charcoal, hydrogen, sodium, or potassium, at comparatively low temperatures. When heated in the presence of organic substances, it gives up its oxygen, converting the carbon of the organic body into carbon dioxide, and its hydrogen into water. It dissolves in acids with formation of salts.

Sulphides.—CUPROUS SULPHIDE—*Subsulphide* or *Protosulphide*—Cu_2S—occurs in nature in soft, fusible, gray crystals (*chalcosine* or *copper glance*), and in many double sulphides, among which is a double sulphide of copper and iron, known as *copper pyrites.*

CUPRIC SULPHIDE—*Protosulphide*—CuS—is obtained by treating a solution of a cupric salt with hydrogen sulphide or ammonium sulphydrate. It is almost black when moist, greenish brown when dry. Hot nitric acid oxidizes it to cupric sulphate; hot hydrochloric acid converts it into cupric chloride, with separation of sulphur and formation of hydrogen sulphide. It is sparingly soluble in ammonium sulphydrate, its solubility being increased by the presence of organic matter.

Chlorides.—CUPROUS CHLORIDE—*Subchloride* or *Protochloride*—Cu_2Cl_2—is prepared by heating copper with one of the chlorides of mercury;

by dissolving cuprous oxide in hydrochloric acid without contact of air; or by the action of reducing agents upon solutions of cupric chloride. It is a heavy, white powder; turns violet and blue by exposure to light; soluble in concentrated hydrochloric acid, insoluble in water. It forms a crystallizable compound with carbon monoxide, and its solution in hydrochloric acid is used in analysis to absorb that gas.

CUPRIC CHLORIDE—*Chloride* or *Deutochloride*—$CuCl_2$—is formed by dissolving copper in aqua regia; if copper be present in excess, it reduces the cupric to cuprous chloride. It crystallizes in bluish green, rhombic prisms with 2 Aq., deliquescent, very soluble in water and in alcohol.

Salts.—NITRATES.—Cuprous nitrate is unknown. *Cupric nitrate*, $(NO_3)_2Cu$—is formed by dissolving copper, or its oxide, or carbonate in nitric acid. It crystallizes at 20° to 25° with 3 Aq.; below 20° with 6 Aq.

SULPHATES.—The existence of cuprous sulphate is doubtful. *Cupric sulphate—Sulphate of copper—Blue vitriol—Bluestone—Cupri sulphas* (U. S., Br.)—$SO_4Cu+5Aq.$—is prepared: 1st, by roasting copper pyrites; 2d, from the water of copper-mines; 3d, by exposing copper, moistened with dilute sulphuric acid, to air; 4th, by heating copper with concentrated sulphuric acid.

As ordinarily crystallized, it is in fine, blue, oblique prisms, which require for their solution 2.71 parts of water at 19°; and 0.55 parts at 100°. Insoluble in alcohol. The crystals effloresce in dry air at 15°, losing 2 Aq.; at 100° they still retain 1 Aq., which they lose at 230°, forming a white, amorphous powder. The anhydrous salt, in taking up water, resumes its blue color. Its solutions are blue, acid, styptic, and metallic in taste.

When ammonium hydrate is added to a solution of cupric sulphate, a bluish white precipitate falls, which redissolves in excess of the alkali, to form a deep blue solution; strong alcohol floated over the surface of this solution separates long, right rhombic prisms, having the composition $SO_4Cu,4NH_3+H_2O$, which are very soluble in water; their solution constitutes *ammonio-sulphate of copper* or *aqua sapphirina;* and they exist, mixed with other substances, in the *cuprum ammoniatum* (U. S.).

ARSENITE—*Scheele's green—Mineral green*—is a mixture of cupric arsenite and hydrate; prepared by adding potassium arsenite to solution of cupric sulphate. It is a grass-green powder, insoluble in water; soluble in ammonium hydrate, or in acids. Exceedingly poisonous.

Schweinfurt green—Mitis green or *Paris green*—is the most frequently used, and the most dangerous of the cupro-arsenical pigments. It is prepared by adding a thin paste of neutral cupric acetate with water to a boiling solution of arsenious acid, and continuing the boiling during a further addition of acetic acid. It is an insoluble, green, crystalline powder, having the composition $(C_2H_3O_2)_2Cu+3(As_2O_4Cu)$. It is decomposed by prolonged boiling in water, by aqueous solutions of the alkalies, and by the mineral acids.

CARBONATES.—The existence of cuprous carbonate is doubtful. *Cupric carbonate*—CO_3Cu—exists in nature, but has not been obtained artificially. *Dicupric carbonate*—CO_3Cu,CuH_2O_2—exists in nature as *malachite.* When a solution of a cupric salt is decomposed by an alkaline carbonate, a bluish precipitate, having the composition $CO_3Cu,CuH_2O_2+H_2O$, is formed, which, on drying, loses H_2O, and becomes green; it is used as a pigment under the name *mineral green. Tricupric carbonate—Sesquicarbonate of copper*—$2(CO_3Cu),CuH_2O_2$—exists in nature as a blue

mineral called *azurite* or *mountain blue*, and is prepared by a secret process for use as a pigment known as *blue ash*.

ACETATES.—*Cupric acetate—Diacetate—Crystals of Venus*—$(C_2H_3O_2)_2Cu+Aq.$—is formed when cupric oxide or verdigris is dissolved in acetic acid; or by decomposition of solution of cupric sulphate by lead acetate. It crystallizes in large, bluish green prisms, with 1 Aq., which they lose at 140°; when heated to 240° or 260° they are decomposed, with liberation of glacial acetic acid.

Basic acetates.—Verdigris—Cupri subacetas (U. S.)—is a substance prepared by exposing to air piles composed of alternate layers of grape-skins and plates of copper, and removing the bluish green coating from the copper. It is a mixture, in varying proportions, of three different substances: $(C_2H_3O_2)_2Cu,CuH_2O_2 + 5Aq.$; $[(C_2H_3O_2)_2Cu]_2,CuH_2O_2 + 5Aq.$; and $(C_2H_3O_2)_2Cu,2(CuH_2O_2)$.

Analytical characters.—CUPROUS—are very unstable and readily converted into cupric compounds. *Potash*, white precipitate, turning brownish. *Ammonium hydrate*, in absence of air, a colorless liquid; turns blue on exposure to air.

CUPRIC.—White when anhydrous; when soluble in water they form blue or green acid solutions. *Hydrogen sulphide*, black precipitate, insoluble in potassium or sodium sulphide, sparingly soluble in ammonium sulphydrate; soluble in hot concentrated nitric acid and in potassium cyanide. *Alkaline sulphides*, same as hydrogen sulphide. *Potassium* or *sodium hydrate*, pale blue precipitate, insoluble in excess. If the solution be heated over the precipitate, the latter contracts and turns black. *Ammonium hydrate*, in very small quantity, pale blue precipitate; with larger quantities a deep blue liquid. *Potassium or sodium carbonate*, greenish blue precipitate, insoluble in excess, and turning black when the liquid is boiled. *Ammonium carbonate*, pale blue precipitate, soluble with deep blue color in excess. *Potassium cyanide*, greenish yellow precipitate, soluble in excess. *Potassium ferrocyanide*, chestnut-brown precipitate, insoluble in weak acids, decolorized by potash. *Iron* is coated with metallic copper.

Action on the economy.—The opinion, until recently universal among toxicologists, that all the compounds of copper are poisonous, has been much modified by recent researches. Certain of the copper compounds, such as the sulphate, having a tendency to combine with albuminoid and other animal substances, produce symptoms of irritation by their direct local action when brought in contact with the gastric or intestinal mucous membrane. One of the characteristic symptoms of such irritation is the vomiting of a greenish matter, which develops a blue color upon the addition of ammonium hydrate.

Cases are not wanting in which severe illness, and even death, has followed the use of food which has been in contact with imperfectly tinned copper vessels; cases in which nervous and other symptoms referable to a truly poisonous action have occurred. As, however, it has also been shown that non-irritant, *pure* copper compounds may be taken in considerable doses with impunity, it appears at least probable that the poisonous action attributed to copper is due to other substances. The tin and solder used in the manufacture of copper utensils contain lead, and in some cases of so-called copper-poisoning, the symptoms have been such as are as consistent with lead-poisoning as with copper-poisoning. Copper is also notoriously liable to contamination with arsenic, and it is by no means improbable that compounds of that element are the active

poisonous agents in some cases of supposed copper-intoxication. Nor is it improbable that articles of food allowed to remain exposed to air in copper vessels should undergo those peculiar changes which result in the formation of poisonous substances, such us the sausage- or cheese-poisons, or the ptoamines.

The treatment, when irritant copper compounds have been taken, should consist in the administration of white of egg or of milk, with whose albuminoids an inert compound is formed by the copper salt. If vomiting do not occur spontaneously, it should be induced by the usual methods.

The detection of copper in the viscera after death is not without interest, especially if arsenic have been found, in which case its discovery or non-discovery enables us to differentiate between poisoning by the arsenical greens and that by other arsenical compounds. The detection of mere traces of copper is of no significance, because, although copper is not a physiological constituent of the body, it is almost invariably present, having been taken with the food.

Pickles and canned vegetables are sometimes intentionally *greened* by the addition of copper; this fraud is readily detected by inserting a large needle into the pickle or other vegetable; if copper be present the steel will be found to be coated with copper after half an hour's contact.

MERCURY.

Hydrargyrum.....Hg.....200

Commercial mercury is contaminated with other metals. It may be purified by shaking the distilled metal with mercurous nitrate solution, and preserving it under that liquid or strong nitric acid.

It is a bright, metallic liquid; crystallizes at −40°; boils at 360° (350° of the air thermometer); volatilizes slightly at all temperatures above −7°; sp. gr. 13.596. It forms alloys, called *amalgams*, with most other metals; it does not attack iron, and only amalgamates with platinum when heated. If pure, it is not altered in air at the ordinary temperature, but, if impure, is coated with a gray film of mercuric oxide; heated in air to near its boiling point, it is oxidized. It does not decompose water. It combines directly with chlorine, bromine, iodine, and sulphur. Hot, concentrated sulphuric acid dissolves it with evolution of sulphur dioxide, and formation of mercuric sulphate. Nitric acid dissolves it in the cold with formation of a nitrate.

Hydrargyrum cum creta (U. S., Br.) and *Unguentum hydrargyri* (U. S., Br.)—owe their activity to small quantities of mercurous oxide, formed during their preparation; the cause of the greater activity of the latter preparation being due to a more extensive oxidation. It is also probable that the absorption of vapor of mercury by cutaneous surfaces is preceded by its conversion into mercuric chloride.

Oxides.—Mercurous Oxide—*Protoxide* or *black oxide*—Hg_2O—is obtained by adding a solution of mercurous nitrate to an excess of solution of potassium hydrate. It is a brownish black, tasteless powder; very prone to decomposition into mercuric oxide and mercury. Hydrochloric acid converts it into mercurous chloride, and other acids into the corresponding mercurous salts.

It is also formed by the action of calcium hydrate upon mercurous compounds, and exists in the *Lotio hydrargyri nigra* (Br.) or *black wash.*

MERCURIC OXIDE—*Red* or *binoxide—Hydrargyri oxidum flavum* (U. S., Br.)—*Hydrargyri oxidum rubrum* (U. S., Br.)—HgO—is prepared by calcining mercuric nitrate as long as brown fumes are given off; or by precipitating a solution of a mercuric salt by excess of potassium hydrate. The products obtained by these methods, although the same in composition, differ from each other in their physical properties and in the activity of their chemical actions. That obtained by the calcination of the nitrate, *Hydr. oxid. rubrum*, is red and crystalline in structure; that obtained by precipitation, *Hydr. oxid. flavum*, is yellow and amorphous. The latter is much the more active in its chemical and medicinal actions.

Mercuric oxide is very sparingly soluble in water, the solution having a metallic taste and an alkaline reaction. It exists both in solution and in suspension in the *Lotio hydrargyri flava* (Br.) or *yellow wash*, prepared by the action of lime water upon a mercuric salt.

When exposed to air and light it turns black, more rapidly in the presence of organic matter, giving off oxygen and liberating mercury. It is an active oxidizing agent. It decomposes the chlorides of many metallic elements in solution, with formation of a metallic oxide and of mercuric oxychloride; combines with the alkaline chlorides to form soluble double chlorides, *chloromercurates* or *chlorhydrargyrates;* and forms similar compounds with the alkaline iodides and bromides.

Sulphides.—MERCUROUS SULPHIDE — Hg_2S — a very unstable compound, formed by the action of hydrogen sulphide upon mercurous salts.

MERCURIC SULPHIDE — *Red sulphide — Cinnabar — Vermilion — Hydrargyri sulphuretum rubrum* (U. S.)—HgS—exists in nature in amorphous red masses or in red crystals, and is the chief ore of mercury. If sulphur and mercury be ground up together in the cold, or if a solution of a mercuric salt be decomposed by hydrogen sulphide, a black sulphide is formed, which is the *Æthiops mineralis* of the older pharmacists.

A red sulphide is obtained in the arts for use as a pigment (*vermilion*), by agitating for some hours at 60° a mixture of mercury, sulphur, potash, and water. It is a fine, red powder, which turns brown, and finally black, when heated. Heated in air it burns with formation of sulphur dioxide and volatilization of mercury. It is decomposed by strong sulphuric acid, but not by nitric or hydrochloric acids.

Chlorides.—MERCUROUS CHLORIDE—*Protochloride—Mild chloride—Calomel — Hydrargyri chloridum mite* (U. S.) — *Hydrargyri subchloridum* (Br.)—Hg_2Cl_2—is now principally obtained by the mutual decomposition of sodium chloride and mercurous sulphate. Mercuric sulphate is obtained by heating together 2 parts of mercury and 3 parts of sulphuric acid; this is then caused to combine with an equal amount of mercury to that first used, to form mercurous sulphate; which is mixed with dried sodium chloride, and the mixture heated in glass vessels, connected with condensing chambers.

In practice, varying quantities of mercuric chloride are also formed, and must be removed from the product by washing with boiled, distilled water until the washings no longer precipitate with ammonium hydrate. The presence of mercuric chloride in calomel may be detected by the formation of a black stain upon a bright iron surface, immersed in the calomel, moistened with alcohol; or by the production of a black color by

hydrogen sulphide in water which has been in contact with and filtered from calomel so contaminated.

Calomel is also formed in a number of other reactions: 1st, by the action of chlorine upon excess of mercury; 2d, by the action of mercury upon ferric chloride; 3d, by the action of hydrochloric acid, or of a chloride, upon mercurous oxide, or upon a mercurous salt; 4th, by the action of reducing agents, including mercury, upon mercuric chloride.

Calomel crystallizes in nature, and when sublimed, in quadratic prisms; when precipitated it is deposited as a heavy, amorphous, white powder, faintly yellowish, and producing a yellowish mark when rubbed upon a dark suface. It sublimes, without fusing, between 420° and 500°; is insoluble in cold water and in alcohol; soluble in boiling water to the extent of 1 part in 12,000; when boiled with water for some time, it suffers partial decomposition, mercury is deposited and mercuric chloride dissolves.

When exposed to light, calomel becomes yellow, then gray, owing to partial decomposition, with liberation of mercury and formation of mercuric chloride. Chlorine and aqua regia readily convert it into mercuric chloride. Iodine, in the presence of water, converts it into a mixture of mercuric iodide and chloride. Hydrochloric acid and alkaline chlorides convert it into mercuric chloride. This change occurs in the stomach when calomel is taken internally, and that to such an extent when large quantities of chlorides are taken with the food, that calomel cannot be used in naval practice as it may be with patients who do not subsist upon salt provisions. Potassium iodide converts it into mercurous iodide, which is then decomposed, by an excess of alkaline iodide, into mercuric iodide, which dissolves, and mercury. Solutions of the sulphates of sodium, potassium, and ammonium dissolve notable quantities of calomel.

The hydrates and carbonates of sodium and potassium decompose it with formation of mercurous oxide, which is decomposed into mercuric oxide and mercury; if alkaline chlorides be also present, they react upon the mercuric oxide, thus produced, with formation of mercuric chloride.

MERCURIC CHLORIDE—*Perchloride* or *bichloride*—*Corrosive sublimate*—*Hydrargyri chloridum corrosivum* (U. S.)—*Hydrargyri perchloridum* (Br.)—$HgCl_2$—is prepared by heating a mixture of 5 parts of dry mercuric sulphate with 5 parts of dry sodium chloride and 1 part of manganese dioxide in a glass vessel communicating with a condensing chamber.

It crystallizes by sublimation in rectangular octahedra, and by evaporation of its solutions in flattened, right rhombic prisms; fuses at about 265°, and boils at about 295°; 100 parts of water dissolve 6.57 parts of mercuric chloride at 10°, and 53.96 parts at 100°; cold alcohol dissolves it to the extent of 40 per cent. of its weight. It is also soluble in ether, and very soluble in hot hydrochloric acid, which latter solution gelatinizes on cooling. Its solutions have a disagreeable, acid, styptic taste, and are highly poisonous.

It is easily reduced to calomel and elementary mercury, and its aqueous solutions are so decomposed when exposed to light, a change which is retarded by the presence of sodium chloride. When heated with mercury it is converted into mercurous chloride. Zinc, cadmium, nickel, iron, lead, copper, and bismuth remove a part or all of its chlorine, with separation of calomel or of mercury, when they are heated with dry mercuric chloride or with its solution. Hydrogen sulphide decomposes it with separation of a yellow sulpho-chloride, which, with an excess of the gas, is converted into the black mercuric sulphide. It is soluble without decom-

position in sulphuric, nitric, and hydrochloric acids. Hydrates of sodium and potassium decompose it, with separation of a reddish brown oxychloride if added in sufficient quantity, or of the orange-colored mercuric oxide if an excess of the precipitant be used. The hydrates of calcium and magnesium effect a similar decomposition, which does not, however, take place in the presence of an alkaline chloride or of certain organic matters, such as sugar and gum. Many organic substances decompose it into calomel and mercury, especially under the influence of sunlight. Albumen forms with it a white precipitate, which is insoluble in water, but soluble in an excess of fluid albumen and in solutions of alkaline chlorides. It readily combines with metallic chlorides to form soluble double salts, or *chloromercurates*. One of these, obtained in flattened, rhombic prisms by the cooling of a boiling solution of mercuric chloride and ammonium chloride, has the composition $HgCl_2,2(NH_4Cl)+Aq.$, and was formerly known as *sal alembroth* or *sal sapientiæ*.

MERCURAMMONIUM CHLORIDE—*Mercury chloramidide—Infusible white precipitate—Ammoniated mercury—Hydrargyrum ammoniatum* (U. S., Br.)—NH_2HgCl—is prepared by adding a slight excess of ammonium hydrate solution to a solution of mercuric chloride. It is a white powder, insoluble in alcohol, ether, and cold water; decomposed by hot water with separation of a heavy, yellow powder. It is entirely volatile without fusion. The *fusible white precipitate* is formed in small crystals when a solution containing equal parts of mercuric chloride and ammonium chloride is decomposed by sodium carbonate. It is *mercurdiammonium chloride*, NH_2HgCl,NH_4Cl.

Iodides.—MERCUROUS IODIDE—*Protoiodide* or *yellow iodide—Hydrargyri iodidum viride* (U. S., Br)—Hg_2I_2—is prepared by grinding together 200 parts of murcury and 127 parts of iodine with a little alcohol until a green paste is formed. It is a greenish yellow, amorphous powder, insoluble in water and in alcohol. When heated it turns brown and volatilizes completely. When exposed to light, or even after a time in the dark, it is decomposed into mercuric iodide and mercury. The same decomposition is brought about instantly by potassium iodide; more slowly by solutions of alkaline chlorides and by hydrochloric acid when heated. Ammonium hydrate dissolves it with separation of a gray precipitate.

MERCURIC IODIDE—*Biniodide* or *red iodide—Hydrargyri iodidum rubrum* (U. S., Br.)—HgI_2—is obtained by double decomposition between mercuric chloride and potassium iodide, care being had to avoid too great an excess of the alkaline iodide, that the soluble potassium iodhydrargyrate may not be formed.

It is sparingly soluble in water; with alcohol forms colorless solutions. It dissolves readily in many dilute acids and in solutions of ammoniacal salts, alkaline chlorides, and mercuric salts; and in solutions of alkaline iodides. Iron and copper convert it into mercurous iodide, then into mercury. The hydrates of potassium and sodium decompose it into oxide or oxyiodide, and combine with another portion to form iodhydrargyrates, which dissolve. Ammonium hydrate separates from its solution a brown powder, and forms a yellow solution which deposits white flocks.

Cyanides.—MERCURIC CYANIDE—*Hydrargyri cyanidum* (U. S.)—$Hg(CN)_2$—is best prepared by heating together, for a quarter of an hour, potassium ferrocyanide, 1 part; mercuric sulphate, 2 parts; and water 8 parts. It crystallizes in quadrangular prisms; soluble in 8 parts of cold water, much less soluble in alcohol; highly poisonous. When heated dry

it blackens, and is decomposed into cyanogen and mercury; if heated in the presence of moisture it yields hydrocyanic acid, mercury, carbon dioxide, and ammonia. Hot, concentrated sulphuric acid, and hydrochloric, hydrobromic, hydriodic, and sulphydric acids in the cold, decompose it with liberation of hydrocyanic acid. It is not decomposed by alkalies.

Salts.—NITRATES.—There exist, beside the normal mercurous and mercuric nitrates, $(NO_3)_2(Hg_2)$ and $(NO_3)_2Hg$, three basic mercurous nitrates, three basic mercuric nitrates, and a mercuroso-mercuric nitrate.

Mercurous nitrate—$(NO_3)_2(Hg_2)+2Aq$.—is formed when excess of mercury is digested with nitric acid, diluted with one-half vol. of water, until short, prismatic crystals separate.

It effloresces in air; fuses at 70°; dissolves in a small quantity of hot water, but with a larger quantity is decomposed with separation of a yellow basic *trimercuric nitrate*, $(NO_3)_2Hg,2HgO+Aq$.

The *dimercurous nitrate*—$(NO_3)_2(Hg_2),Hg_2O+Aq$.—is formed by acting upon the preceding salt with cold water until it turns lemon-yellow; or by extracting with cold water the residue of evaporation of the product obtained by acting upon excess of mercury with concentrated nitric acid.

A *trimercurous nitrate*—$(NO_3)_4(Hg_2)_2,Hg_2O+3Aq$.—is obtained in large, rhombic prisms, when excess of mercury is boiled with nitric acid, diluted with 5 parts of water, for five to six hours, the loss by evaporation being made up from time to time.

Mercuric nitrate—$(NO_3)_2Hg$—is formed when mercury or mercuric oxide is dissolved in excess of nitric acid, and the solution evaporated at a gentle heat. A sirupy liquid is obtained, which, over quick-lime, deposits large, deliquescent crystals, having the composition $2[(NO_3)_2Hg]+Aq$., while there remains an uncrystallizable liquid, $(NO_3)_2Hg+2Aq$.

This salt is soluble in water and exists in the *Liq. hydrargyri nitratis* (U. S.) or *Liq. hydrargyri nitratis acidus* (Br.); in the volumetric standard solution used in Liebig's process for urea; and probably in *citrine ointment*, *Unguentum hydrargyri nitratis* (U. S., Br.).

Dimercuric nitrate—$(NO_3)_2Hg,HgO+Aq$.—is formed when mercuric oxide is dissolved to saturation in hot nitric acid, diluted with its volume of water. It crystallizes on cooling in needles; is decomposed by water into *trimercuric nitrate*, $(NO_3)_2Hg.2HgO$, and neutral mercuric nitrate.

A *hexamercuric nitrate*—$(NO_3)_2Hg,5HgO$—is also formed, as a red powder, by the action of water upon trimercuric nitrate.

Sulphates.—MERCUROUS and MERCURIC SULPHATES—$SO_4(Hg_2)$ and SO_4Hg—are crystalline compounds, which are formed as a step in the preparation of mercurous and mercuric chlorides (*q. v.*).

Analytical characters.—MERCUROUS.—*Hydrochloric acid*, white precipitate, insoluble in water and in acids, except aqua regia; turns black on the addition of ammonium hydrate; when boiled with hydrochloric acid, deposits mercury, while mercuric chloride dissolves. *Hydrogen sulphide*, black precipitate, insoluble in alkaline sulphides, in dilute acids, and in potassium cyanide; partly soluble in boiling nitric acid. *Potassium hydrate*, black precipitate, insoluble in excess. *Potassium iodide*, greenish precipitate, converted by excess into mercury, which remains, and mercuric iodide, which dissolves.

MERCURIC.—*Hydrogen sulphide*, black precipitate. If the reagent be slowly added, the precipitate is first white, then orange, finally black. *Ammonium sulphydrate*, black precipitate, insoluble in excess, except in the presence of organic matter. *Potassium* or *sodium hydrate*, yellow

precipitate, insoluble in excess. *Ammonium hydrate*, white precipitate, soluble in great excess, and in solutions of ammoniacal salts. *Potassium carbonate*, red precipitate. *Potassium iodide*, yellow precipitate, rapidly turning to salmon-colored, then to red; readily soluble in excess of precipitant or in great excess of mercuric salt.

Action on the economy.—Mercury, in the metallic form, is without action upon the animal economy so long as it remains such; on contact, however, with alkaline chlorides it is converted into a soluble double chloride, and this the more readily the greater the degree of subdivision of the metal. The mercurials insoluble in dilute hydrochloric acid are also inert until they are converted into soluble compounds.

Mercuric chloride, a substance into which many other compounds of mercury are converted when taken into the stomach or applied to the skin, not only has a distinctly corrosive action, by virtue of its tendency to unite with albuminoids, but when absorbed it produces well-marked poisonous effects, somewhat similar to those of arsenical poisoning; indeed, owing to its corrosive action and to its greater solubility, and more rapid absorption, it is a more dangerous poison than arsenic trioxide. In poisoning by corrosive sublimate, the symptoms begin sooner after the ingestion of the poison than in arsenical poisoning, and those phemonena referable to the local action of the toxic are more intense.

The treatment should consist in the administration of white of egg, not in too great quantity, and the removal of the compound formed, by emesis, before it has had time to redissolve in the alkaline chlorides contained in the stomach.

Absorbed mercury tends to remain in the system in combination with albuminoids, from which it may be set free, or, more properly, brought into soluble combination, at a period quite removed from the date of last administration, by the administration of alkaline iodides.

Mercury is eliminated principally by the saliva and urine, in which it may be readily detected. The fluid is faintly acidulated with hydrochloric acid, and in it is immersed a short bar of zinc, around which a spiral of dentist's gold-foil is wound in such a way as to expose alternate surfaces of zinc and gold. After 24 hours, if the saliva or urine contain mercury, the gold will be whitened by amalgamation; and, if dried and heated in the closed end of a small glass tube, will give off mercury, which condenses in globules, visible with the aid of a magnifier, in the cold part of the tube.

WEIGHTS AND MEASURES.

1 milligram	= 0.001 gram	=	0.015 gr. Tr.
1 centigram	= 0.01 "	=	0.154 " "
1 decigram	= 0.1 "	=	1.543 " "
1 GRAM		=	15.434 grs. "
1 decagram	= 10 grams	=	154.34 " "
1 hectogram	= 100 "	=	0.268 lb. "
1 kilogram	= 1000 "	=	2.679 lbs. "

1 millimetre	= 0.001 metre	=	0.0394 inch.
1 centimetre	= 0.01 "	=	0.3937 "
1 decimetre	= 0.1 "	=	3.9371 inches.
1 METRE		=	39.3708 "
1 decametre	= 10 metres	=	32.8089 feet.
1 hectometre	= 100 "	=	328.089 "
1 kilometre	= 1000 "	=	0.6214 mile.

1 millilitre, or c.c.	= 0.001 litre	=	0.0021 U. S. pint.
1 centilitre	= 0.01 "	=	0.0211 " "
1 decilitre	= 0.1 "	=	0.2113 " "
1 LITRE		=	1.0567 " quart.
1 decalitre	= 10 litres	=	2.6418 " galls.
1 hectolitre	= 100 "	=	26.418 " "
1 kilolitre	= 1000 "	=	264.18 " "

1 grain	Troy	=	0.0648 gram.
1 ounce	"	=	31.15 grams.
1 "	U. S. P.	=	31.096 "
1 "	Br. P.	=	28.35 "
1 "	Avoird.	=	28.35 "
1 pound	U. S. P.	=	372.115 "
1 "	Br. P.	=	453.6 "

1 inch		=	0.254 metre.
1 foot		=	0.3048 "
1 yard		=	0.9144 "
1 rod		=	5.0799 metres.
1 furlong		=	203.196 "
1 mile		=	1625.568 "

1 minim	U. S. P.	=	0.061 c.c.
1 fluidrachm	"	=	3.7 "
1 fluidounce	"	=	29.6 "
1 pint	"	=	0.47 litre.
1 minim	Br. P.	=	0.058 c.c.
1 fluidrachm	"	=	3.5 "
1 fluidounce	"	=	28.4 "
1 pint	"	=	0.56 litre.

Centigrade to Fahrenheit.

$$\frac{\text{Cent.} \times 9}{5} + 32 = \text{Fahr.}$$

Fahrenheit to Centigrade.

$$\frac{\text{Fahr.} - 32}{9} \times 5 = \text{Cent.}$$

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